Supporting Information
for

Rhodium and Iridium Complexes Bearing "Capping Arene" Ligands: Synthesis and Characterization

Shunyan Gu[†], Charles B. Musgrave III[‡], Zoë M. Gehman[†], Ke Zhang[†], Diane A. Dickie[†], William A. Goddard III, [‡]* and T. Brent Gunnoe[†]*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, United States

Corresponding authors: tbg7h@virginia.edu; wagoddard3@gmail.com

CONTENT

Note that some NMR spectra contain minor impurities due to *n*-pentane and THF. These solvent impurities are due to NMR solvents absorbing minor amounts of chemicals from the glovebox atmosphere.

1. NMR spectra of compounds at room temperature

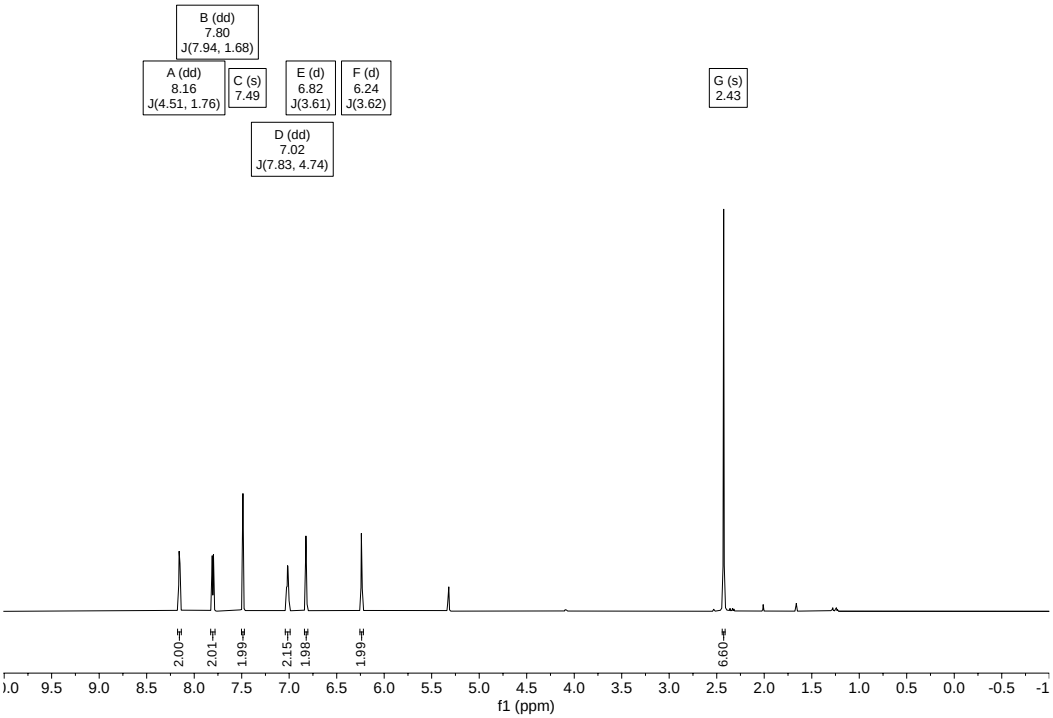

Figure S1. ^{1}H NMR spectrum of 5-^{Me}FP (**3**) in CD_2Cl_2.

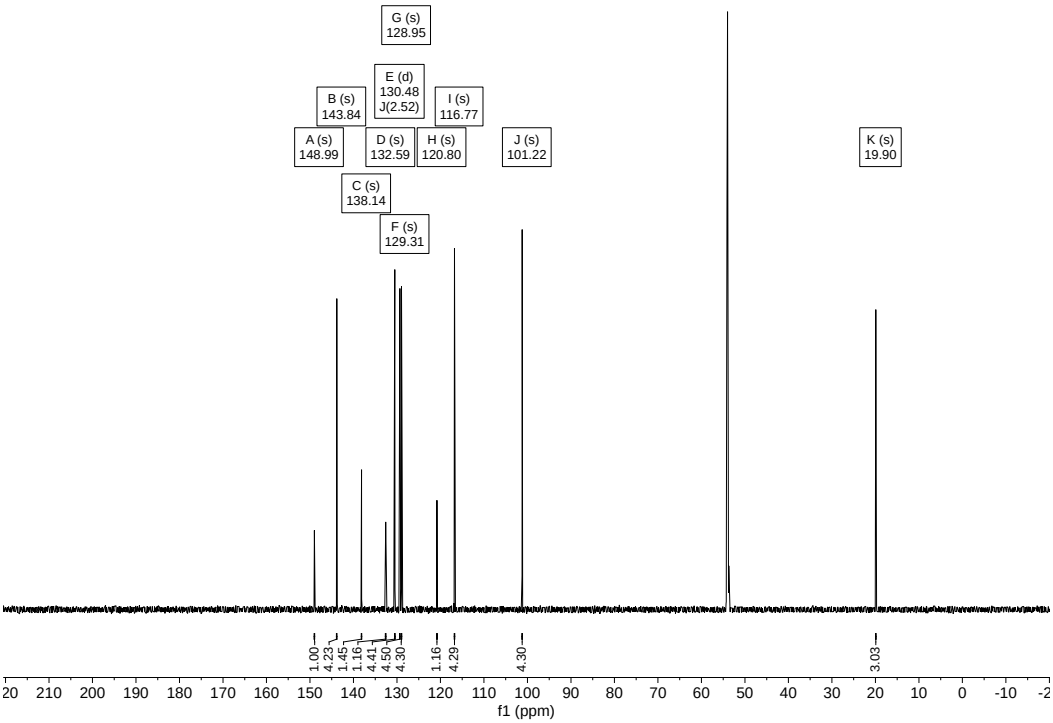

Figure S2. ^{13}C{^{1}H} NMR spectrum of 5-^{Me}FP (**3**) in CD_2Cl_2.

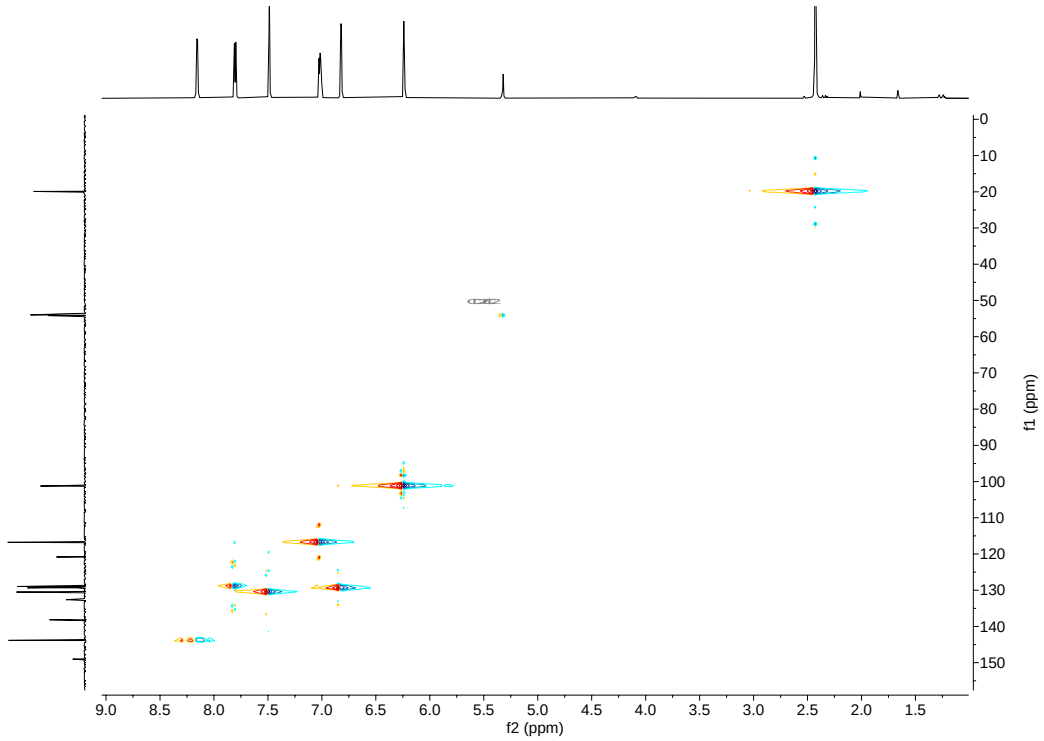

Figure S3. HSQC spectrum of 5-^{Me}FP (**3**) in CD_2Cl_2.

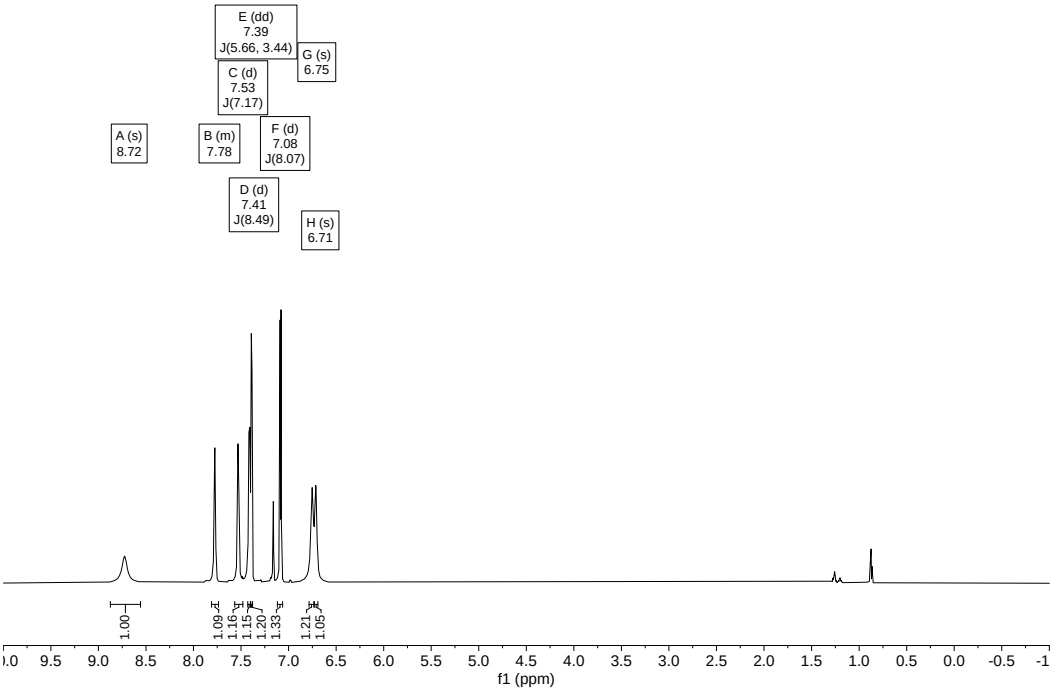

Figure S4. ^{1}H NMR spectrum of 6-FP (**4**) in C_6D_6.

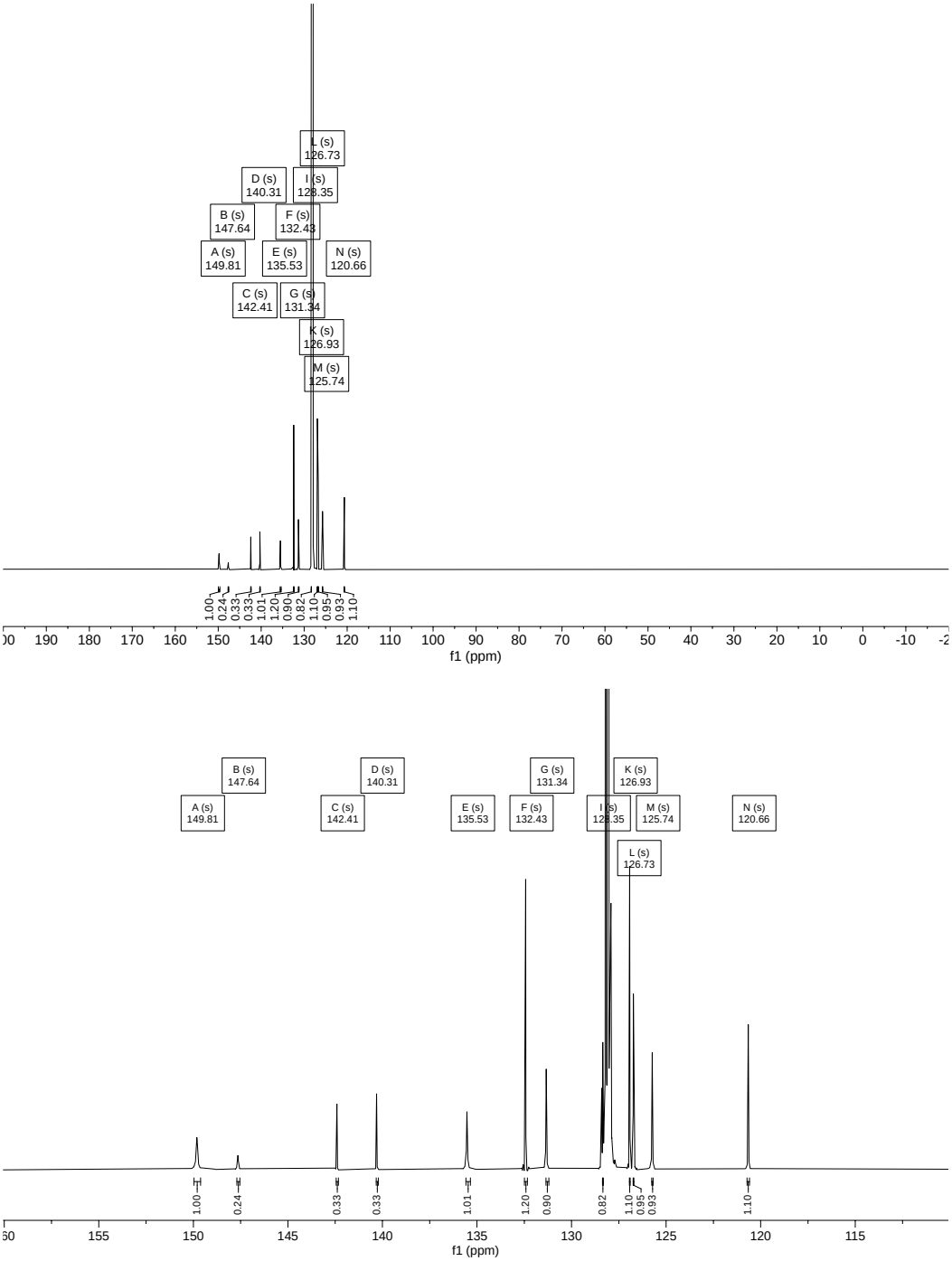

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of 6-FP (**4**) in C_6D_6 (bottom: the aromatic region of the spectrum).

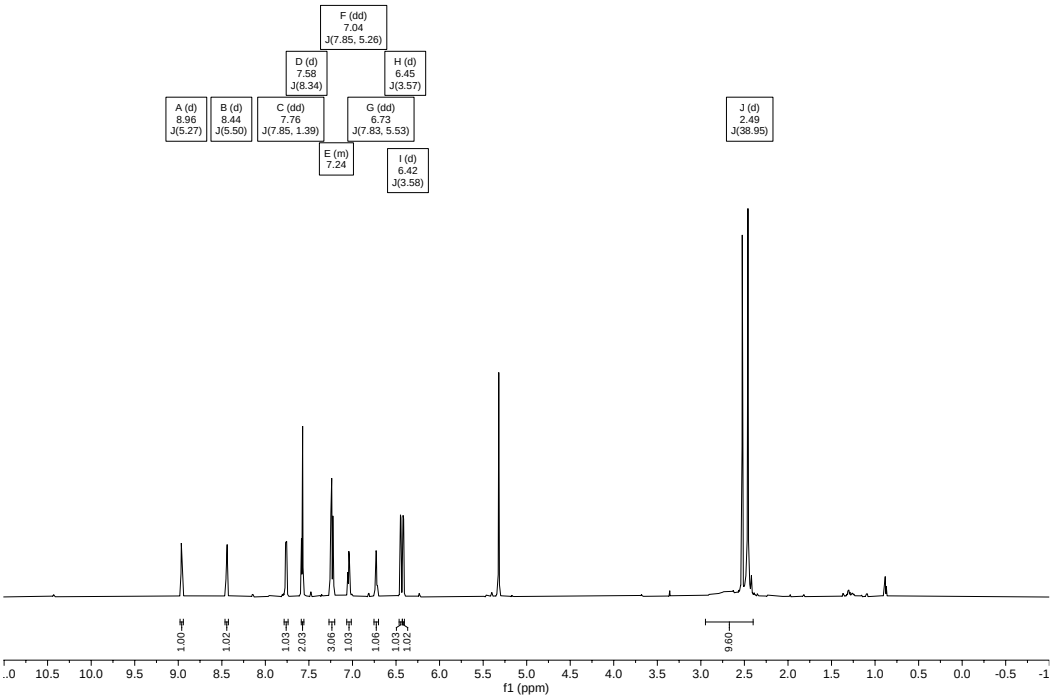

Figure S6. ^{1}H NMR spectrum of (5-^{Me}FP)Rh(C_2H_4)Cl (**3a**) in CD_2Cl_2.

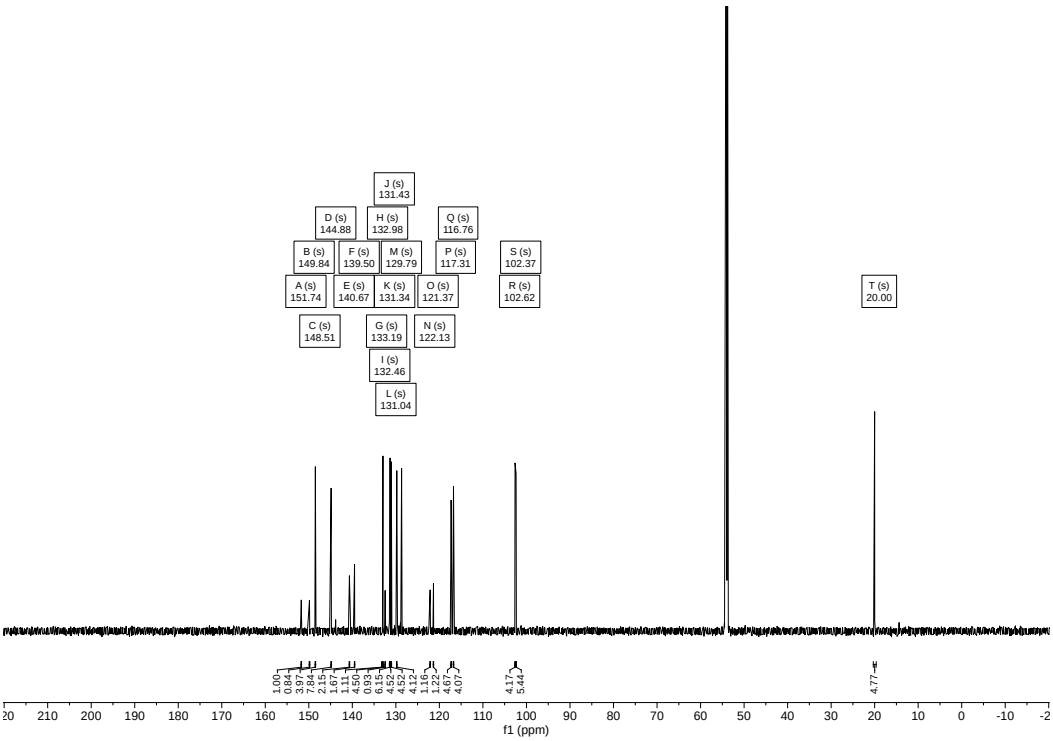

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of (5-^{Me}FP)Rh(C_2H_4)Cl (**3a**) in CD_2Cl_2.

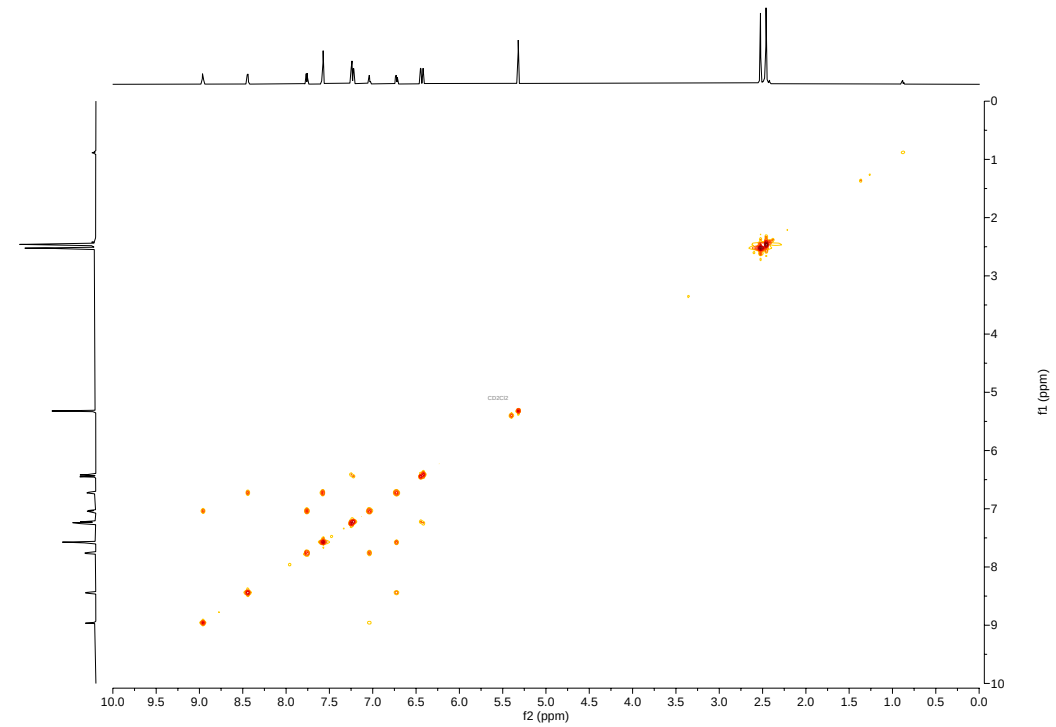

Figure S8. COSY spectrum of (5-^{Me}FP)Rh(C_2H_4)Cl (**3a**) in CD_2Cl_2.

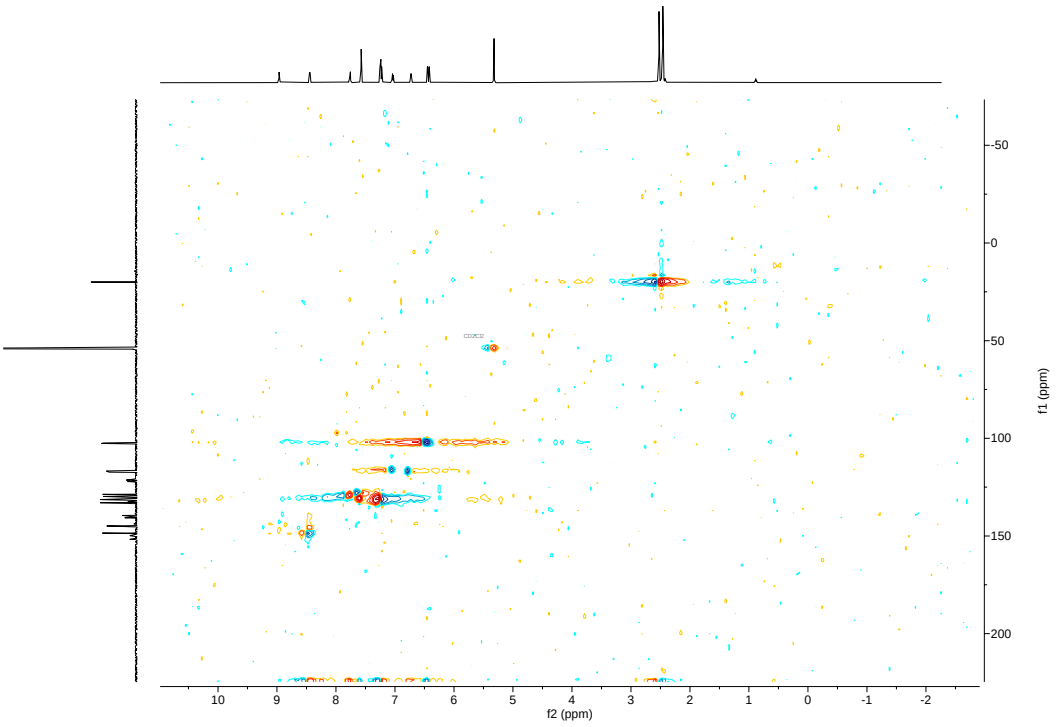

Figure S9. HSQC spectrum of (5-^{Me}FP)Rh(C_2H_4)Cl (**3a**) in CD_2Cl_2.

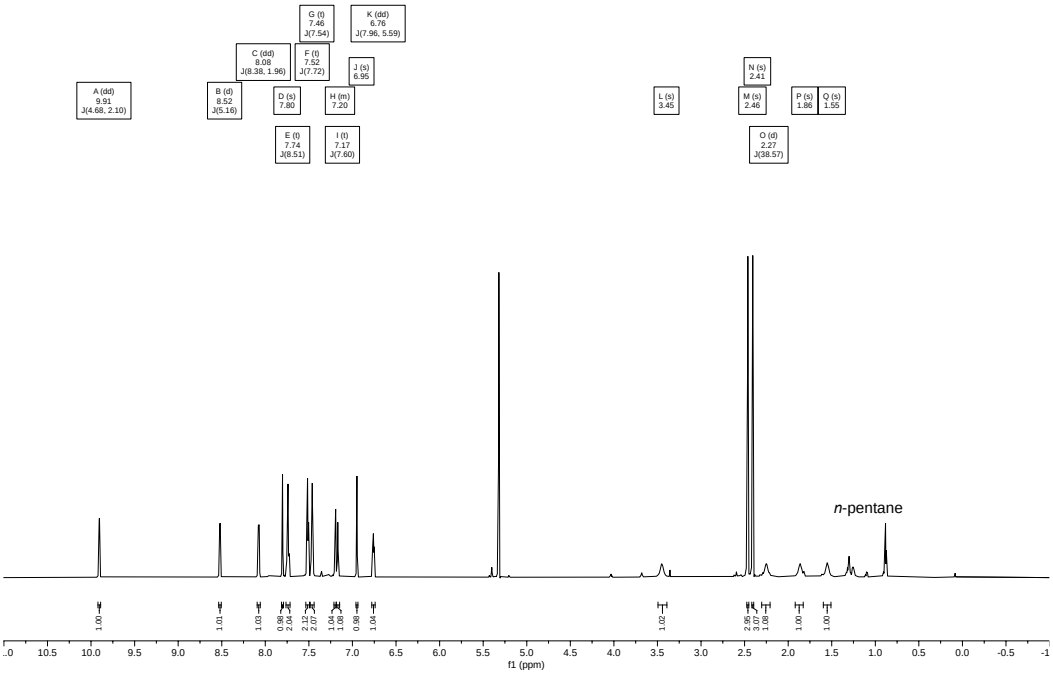

Figure S10. ^{1}H NMR spectrum of (6-^{Me}FP)Rh(C_2H_4)Cl (**6a**) in CD_2Cl_2.

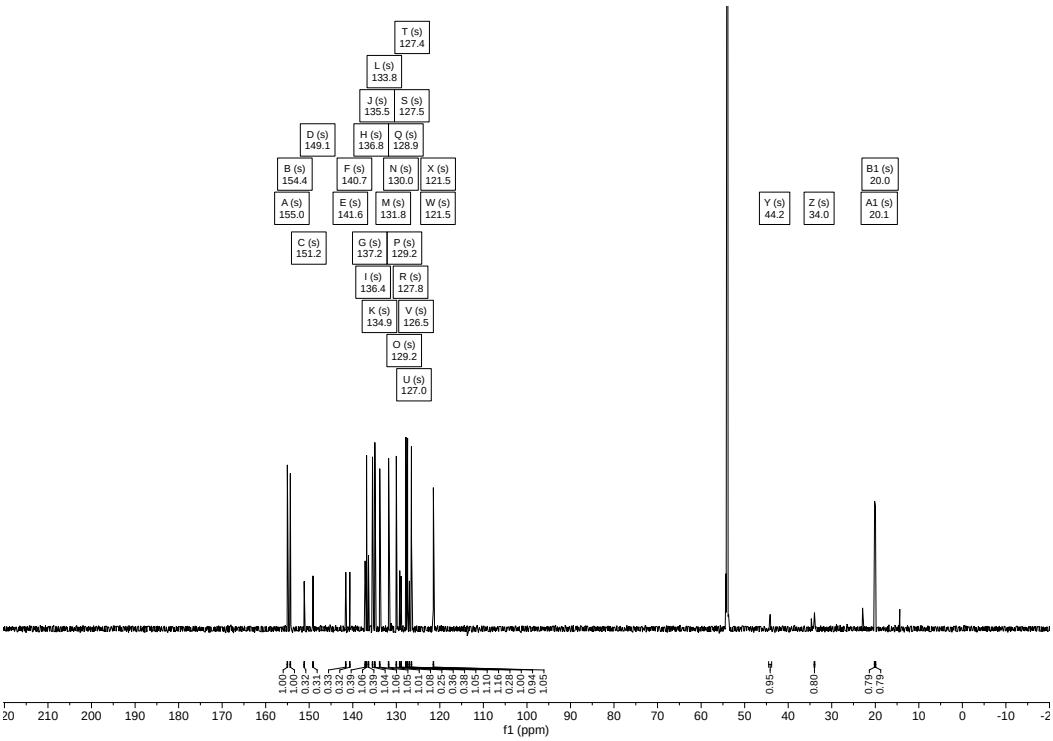

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of (6-^{Me}FP)Rh(C_2H_4)Cl (**6a**) in CD_2Cl_2. *n*-Pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

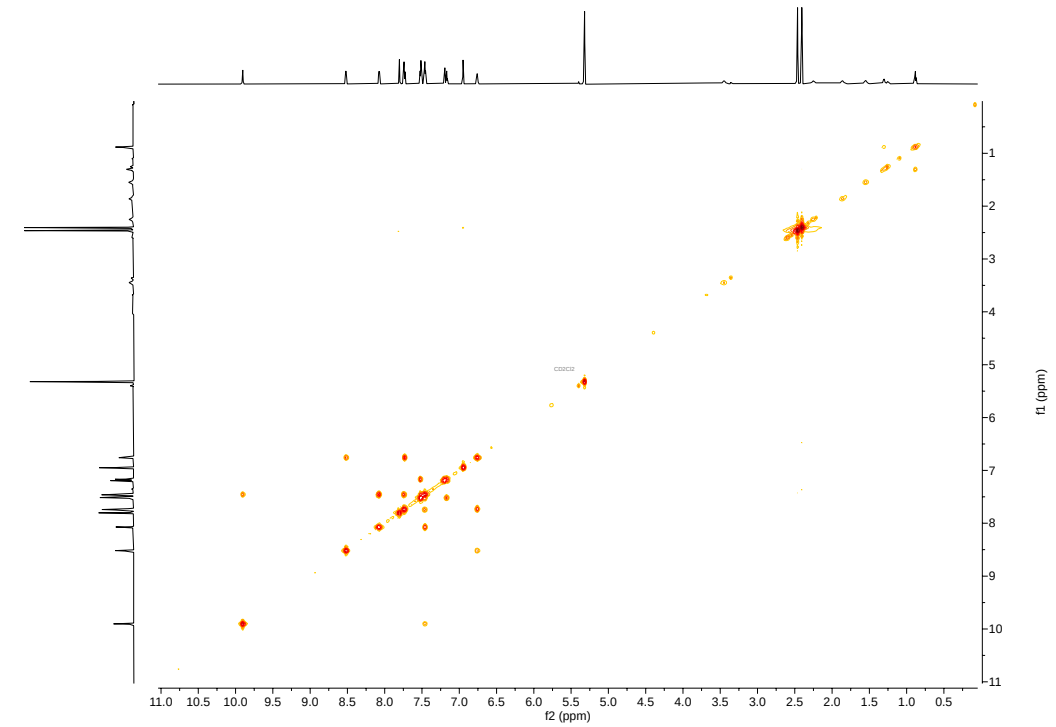

Figure S12. COSY spectrum of (6-^{Me}FP)Rh(C_2H_4)Cl (**6a**) in CD_2Cl_2.

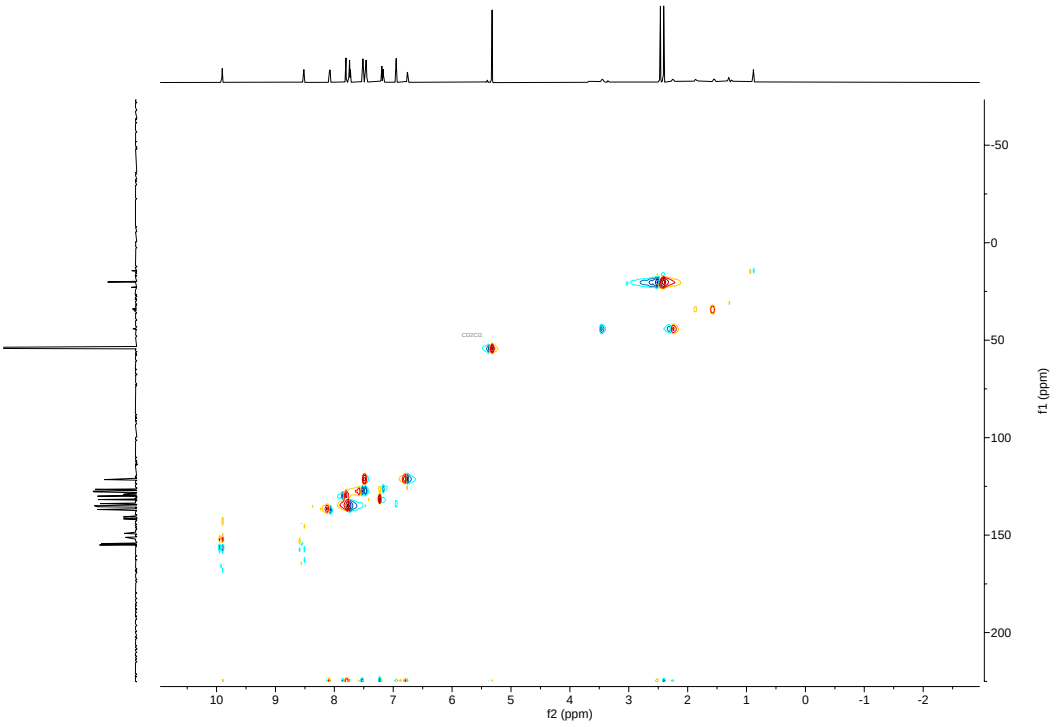

Figure S13. HSQC spectrum of (6-^{Me}FP)Rh(C_2H_4)Cl (**6a**) in CD_2Cl_2.

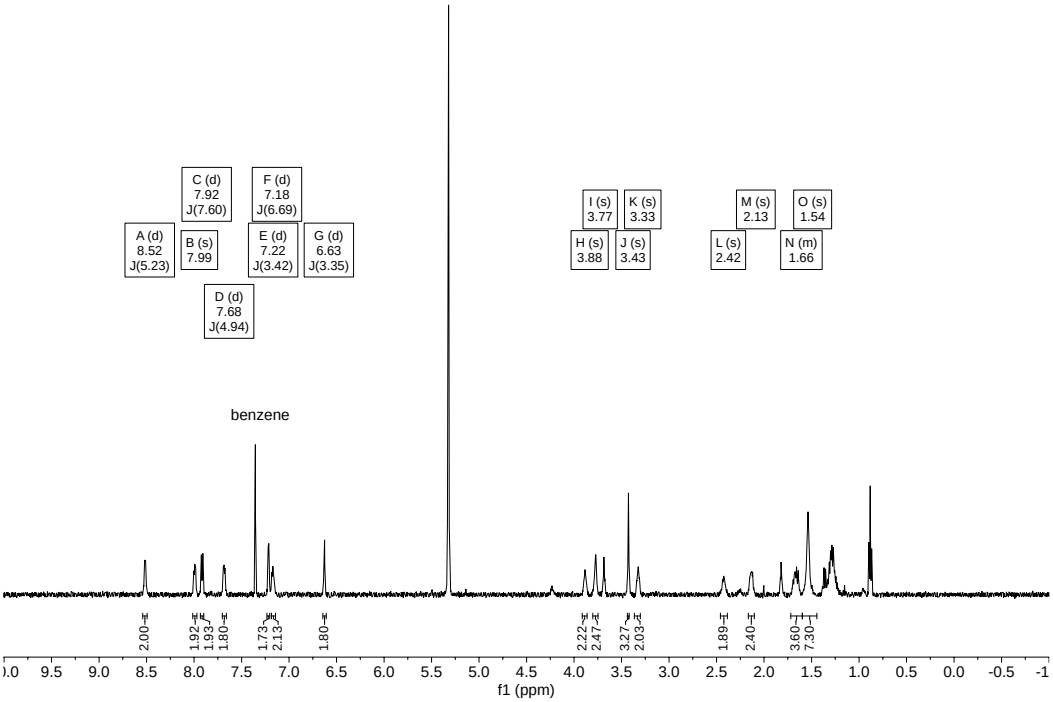

Figure S14. ^{1}H NMR spectrum of [(5-FP)Ir(COD)][Ir(COD)Cl_2] (**1b**) in CD_2Cl_2.

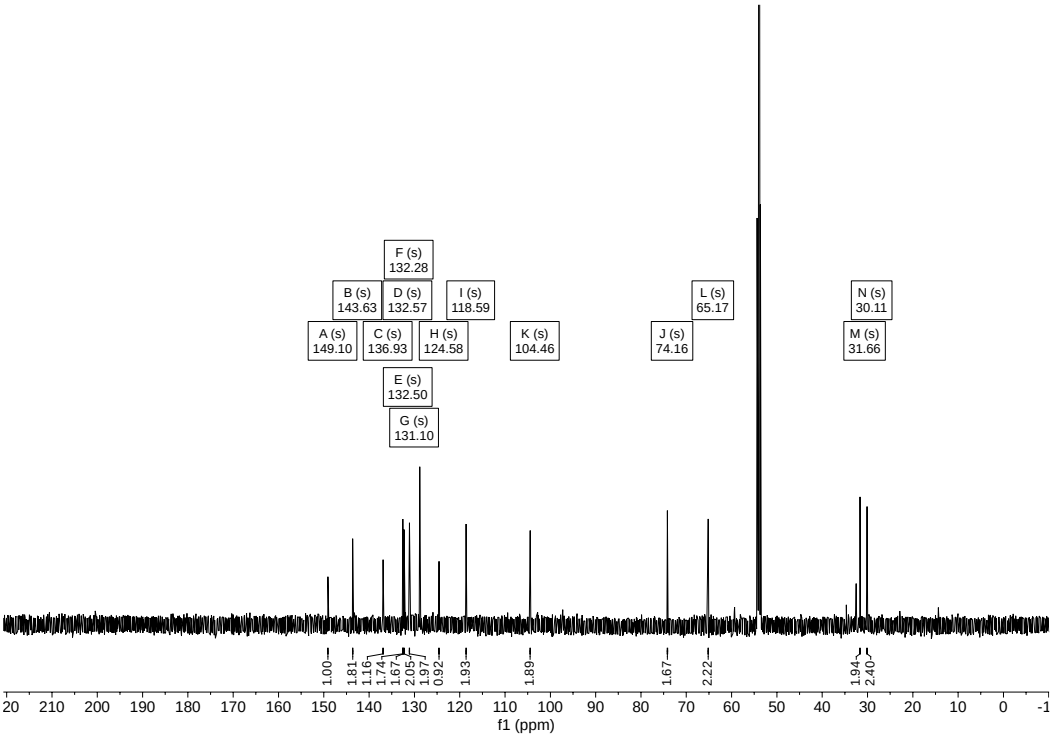

Figure S15. ^{13}C{^{1}H} NMR spectrum of [(5-FP)Ir(COD)][Ir(COD)Cl_2] (**1b**) in CD_2Cl_2. Minor *n*-pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

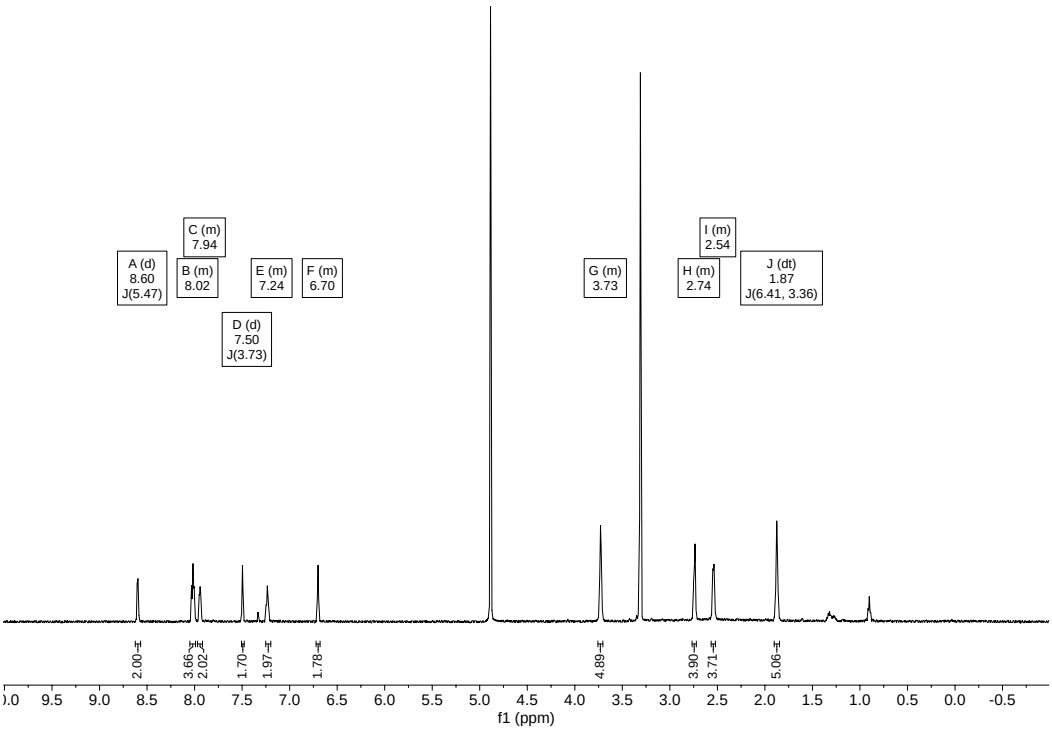

Figure S16. ^{1}H NMR spectrum of $[(5\text{-FP})Ir(C_2H_4)_2][Ir(C_2H_4)_2Cl_2]$ (**1d**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm.

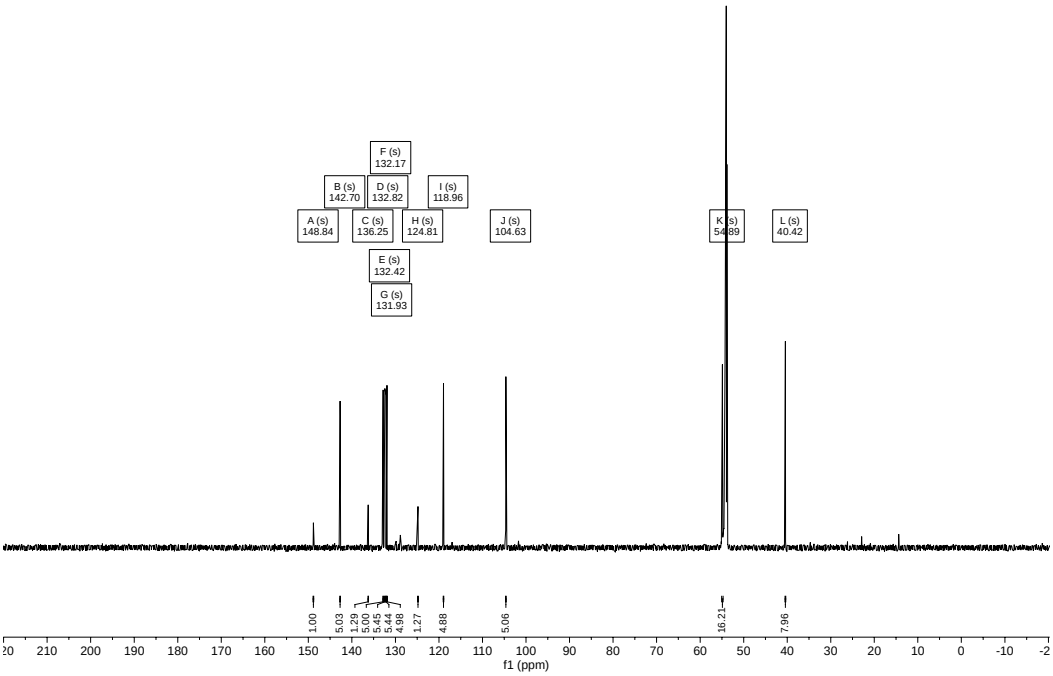

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of $[(5\text{-FP})Ir(C_2H_4)_2][Ir(C_2H_4)_2Cl_2]$ (**1d**) in CD_2Cl_2. Minor *n*-pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

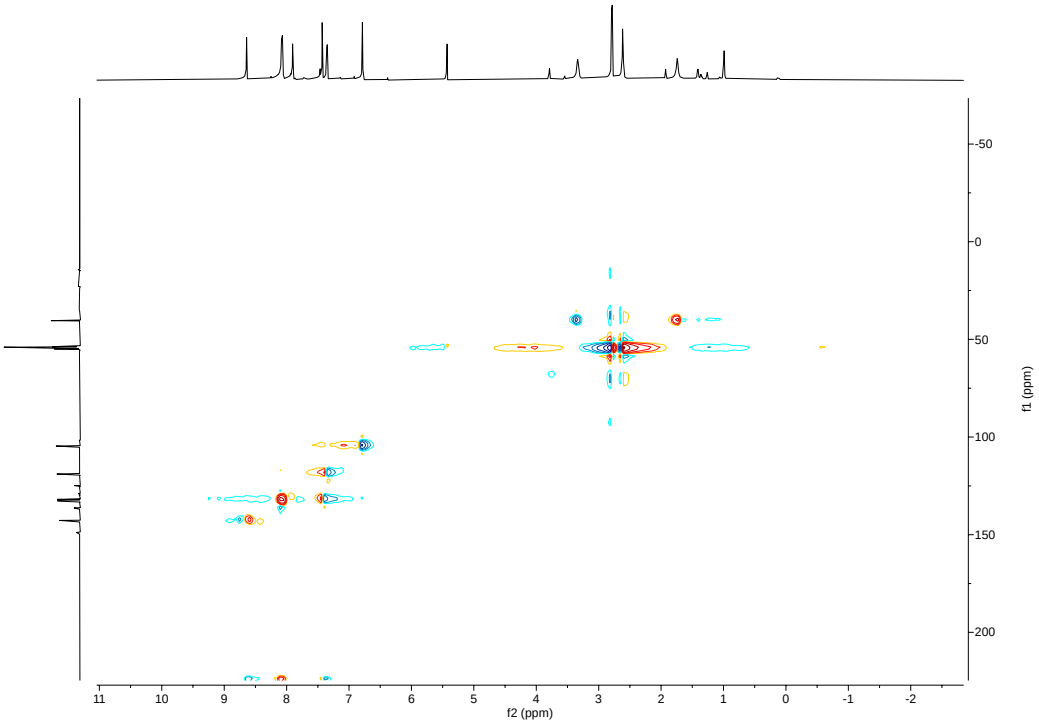

Figure S18. HSQC spectrum of $[(5\text{-FP})Ir(C_2H_4)_2][Ir(C_2H_4)_2Cl_2]$ (**1d**) in CD_2Cl_2.

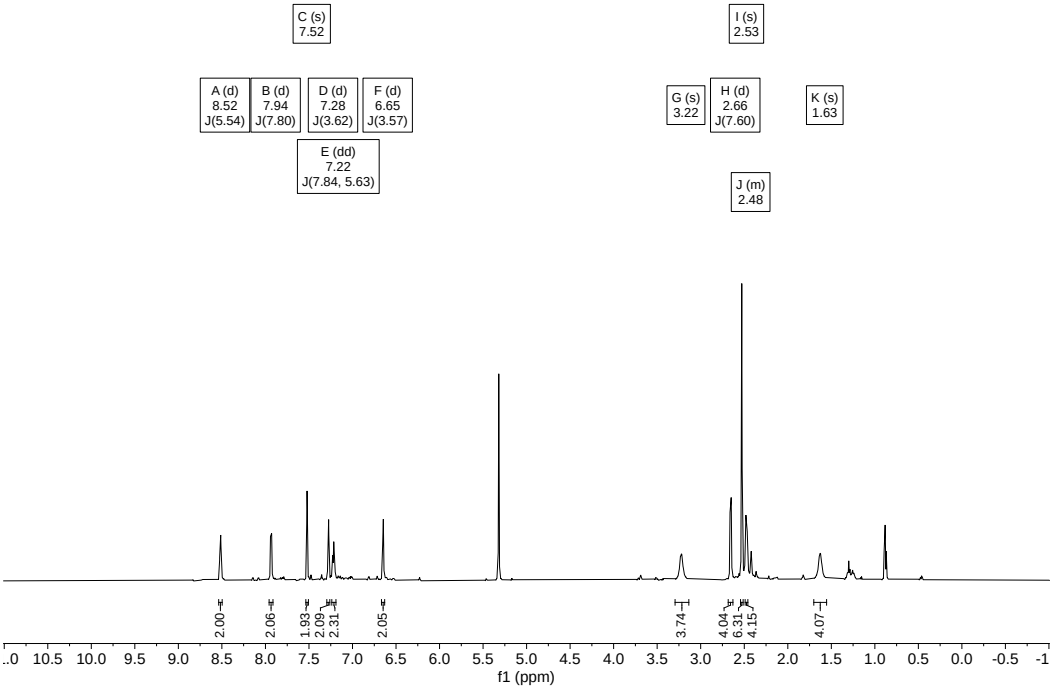

Figure S19. ^{1}H NMR spectrum of $[(5\text{-}^{Me}FP)Ir(C_2H_4)_2][Ir(C_2H_4)_2Cl_2]$ (**3d**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm.

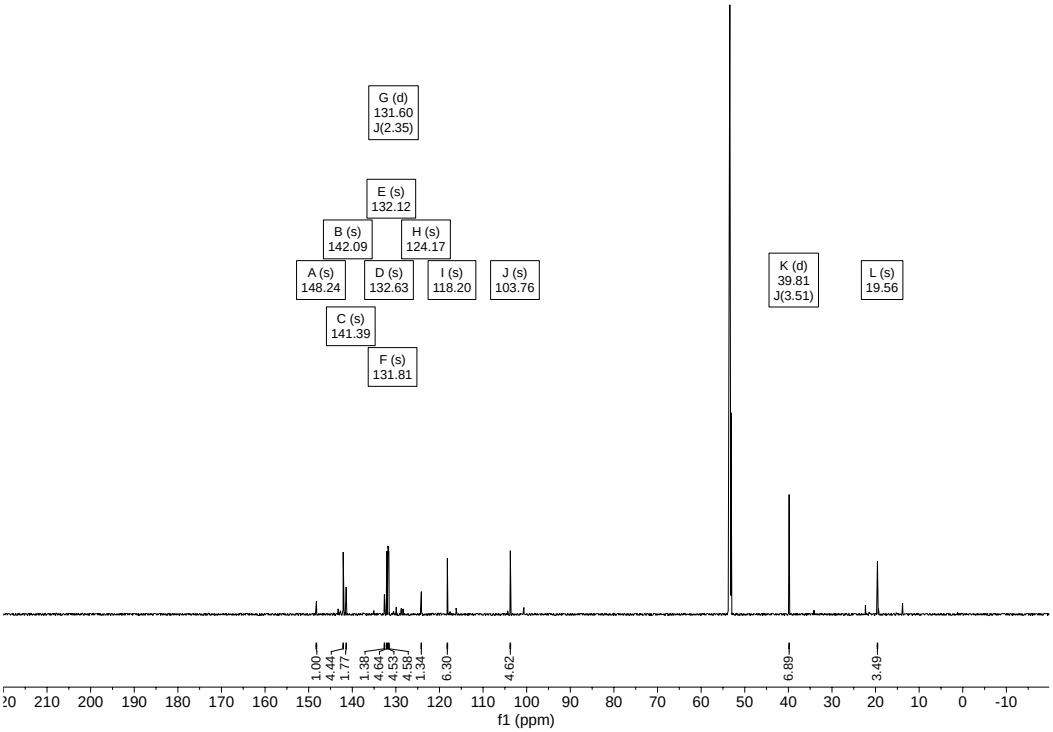

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of [(5-^{Me}FP)Ir(C_2H_4)$_2$][Ir(C_2H_4)$_2$$Cl_2$] (**3d**) in CD_2Cl_2. Minor *n*-pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

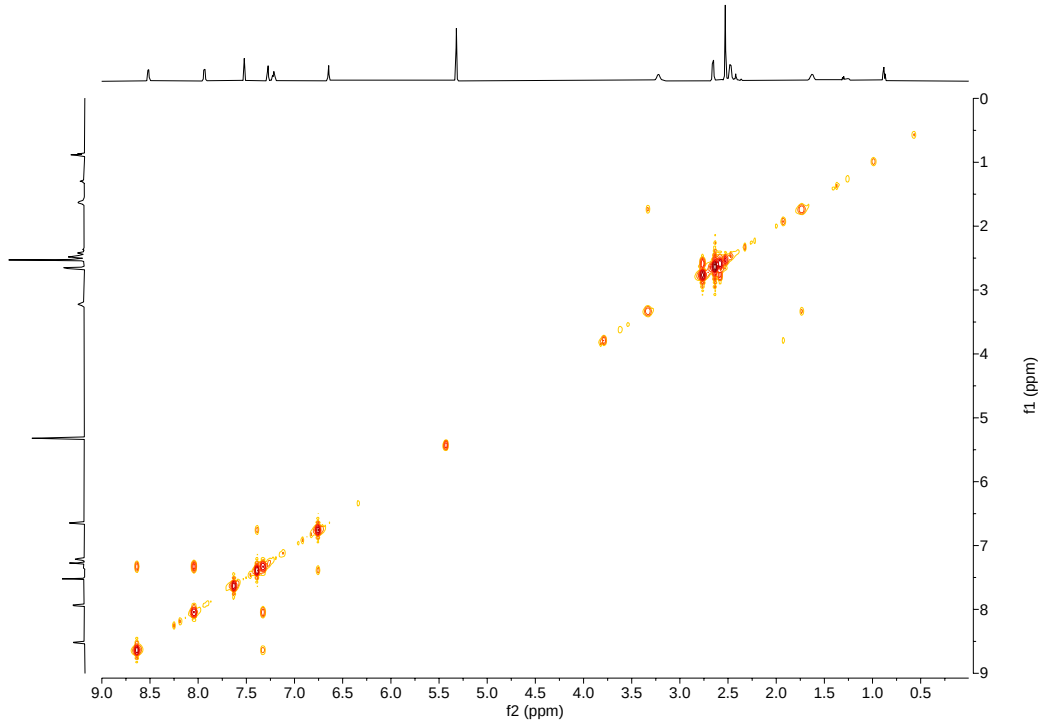

Figure S21. COSY spectrum of [(5-^{Me}FP)Ir(C_2H_4)$_2$][Ir(C_2H_4)$_2$$Cl_2$] (**3d**) in CD_2Cl_2.

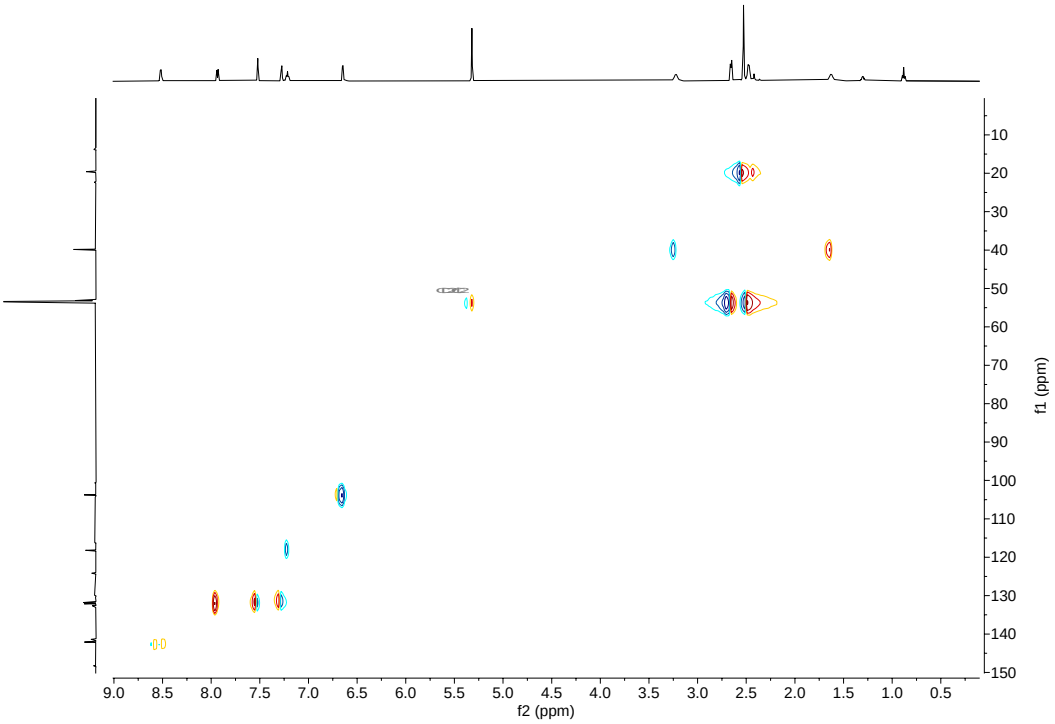

Figure S22. HSQC spectrum of [(5-^{Me}FP)Ir(C_2H_4)$_2$][Ir(C_2H_4)$_2$$Cl_2$] (**3d**) in CD_2Cl_2.

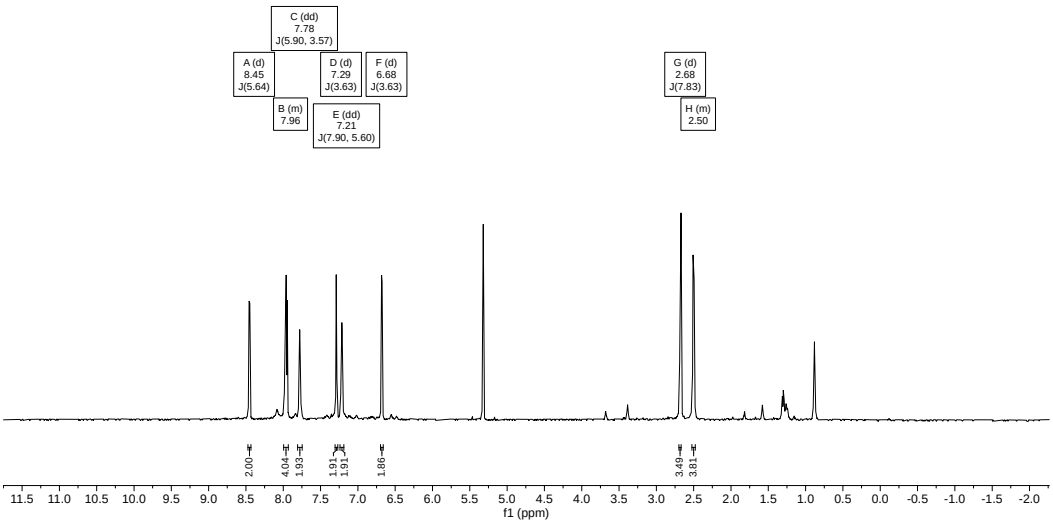

Figure S23. ^{1}H NMR spectrum of [(5-FP)Ir(C_2H_4)$_2$]BF_4 (**1e-BF_4**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm.

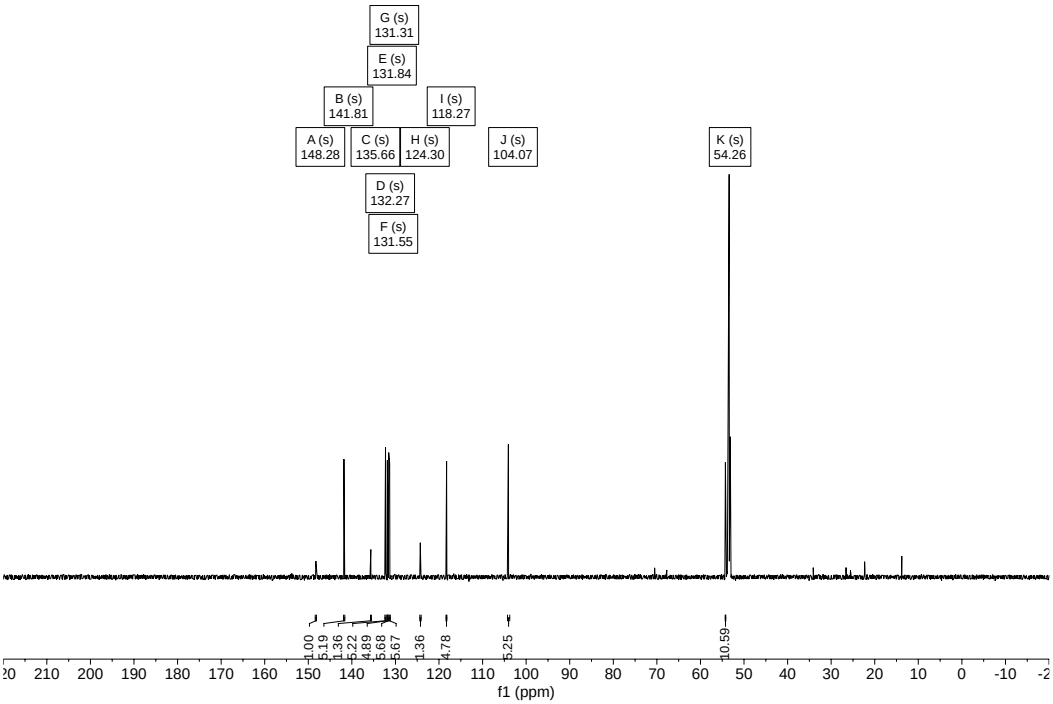

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of $[(5\text{-FP})Ir(C_2H_4)_2]BF_4$ (**1e-BF$_4$**) in CD_2Cl_2. Minor *n*-pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

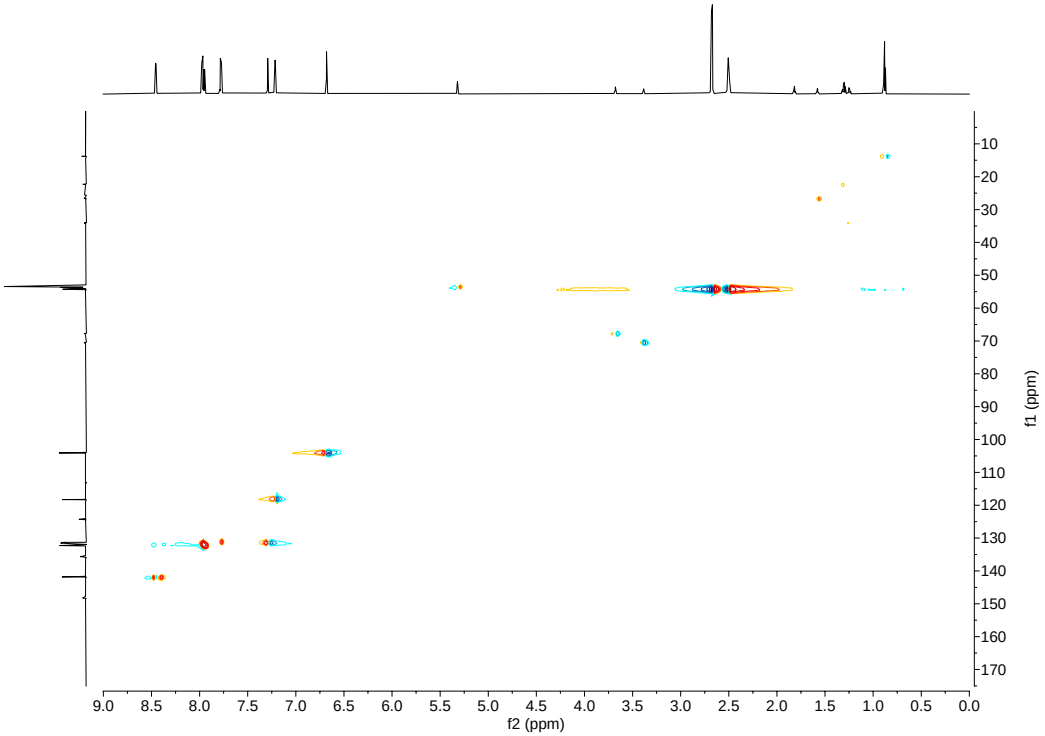

Figure S25. HSQC spectrum of $[(5\text{-FP})Ir(C_2H_4)_2]BF_4$ (**1e-BF$_4$**) in CD_2Cl_2.

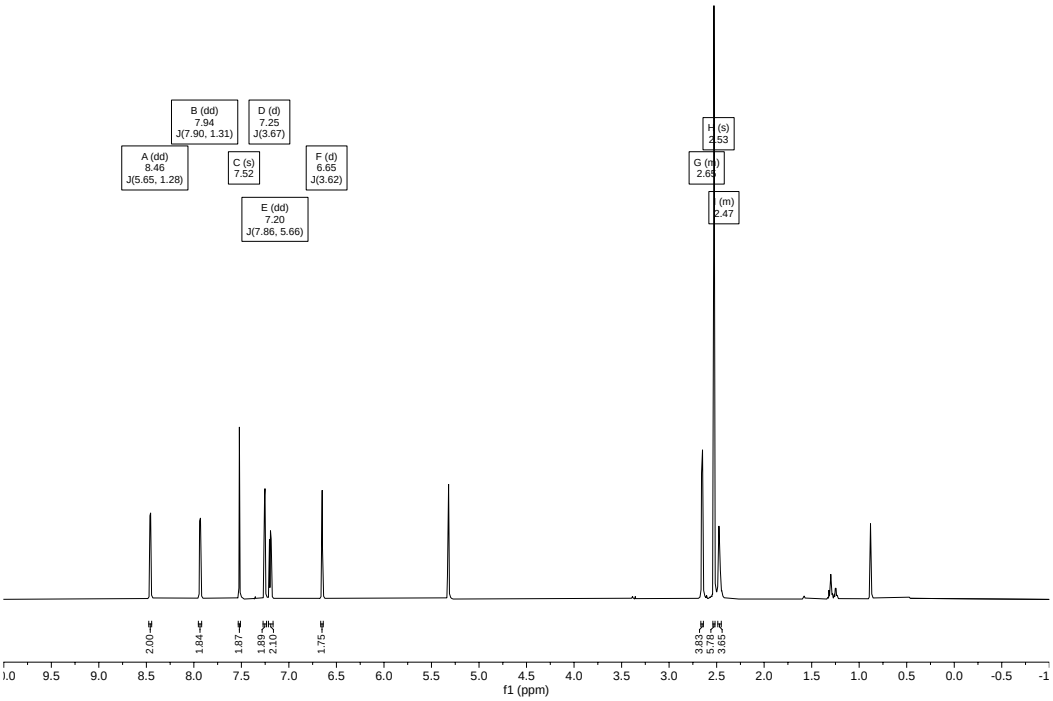

Figure S26. ^{1}H NMR spectrum of $[(5\text{-}^{Me}FP)Ir(C_2H_4)_2]BF_4$ (**3e-BF₄**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm.

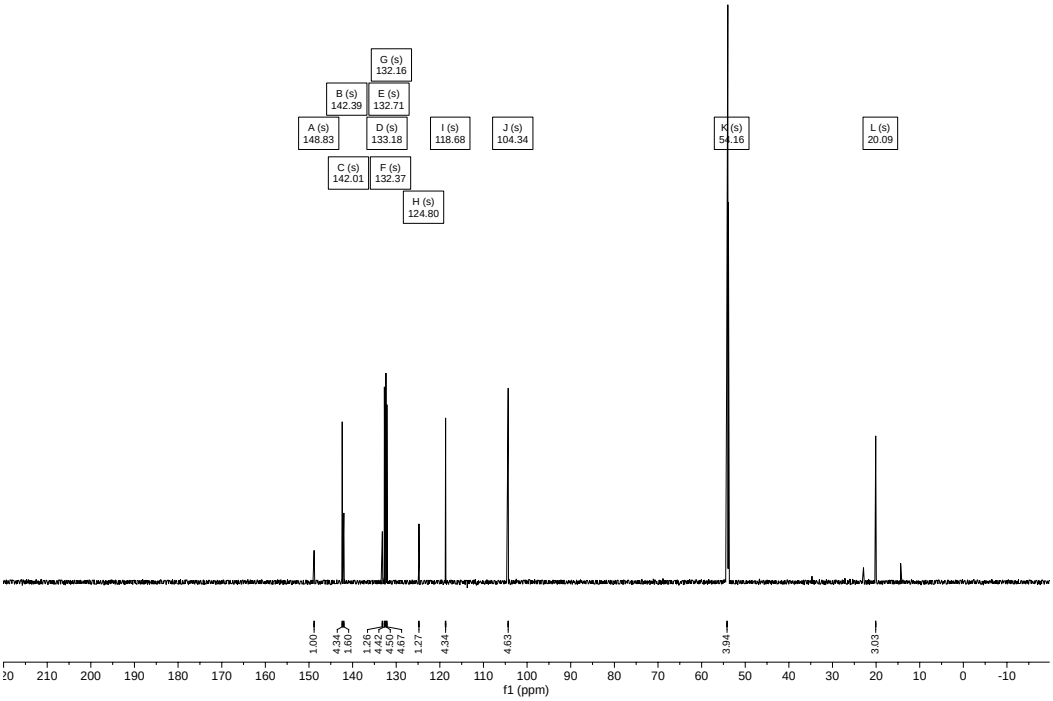

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of $[(5\text{-}^{Me}FP)Ir(C_2H_4)_2]BF_4$ (**3e-BF₄**) in CD_2Cl_2. Minor *n*-pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

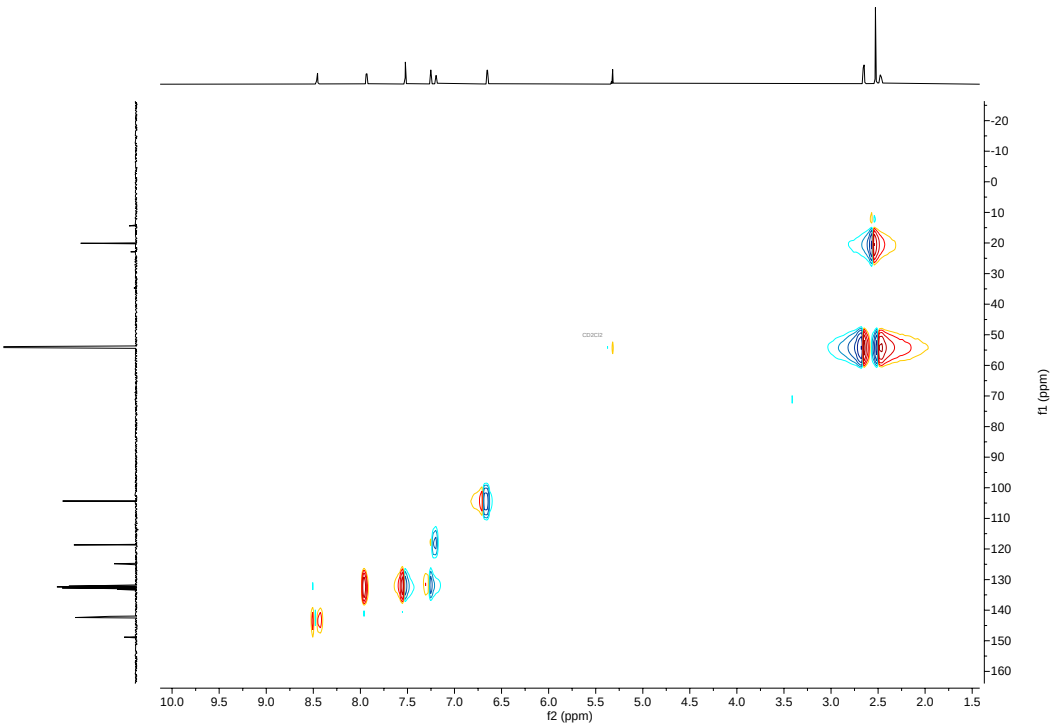

Figure S28. HSQC spectrum of [(5-^{Me}FP)Ir(C_2H_4)$_2$]BF_4 (**3e-BF$_4$**) in CD_2Cl_2.

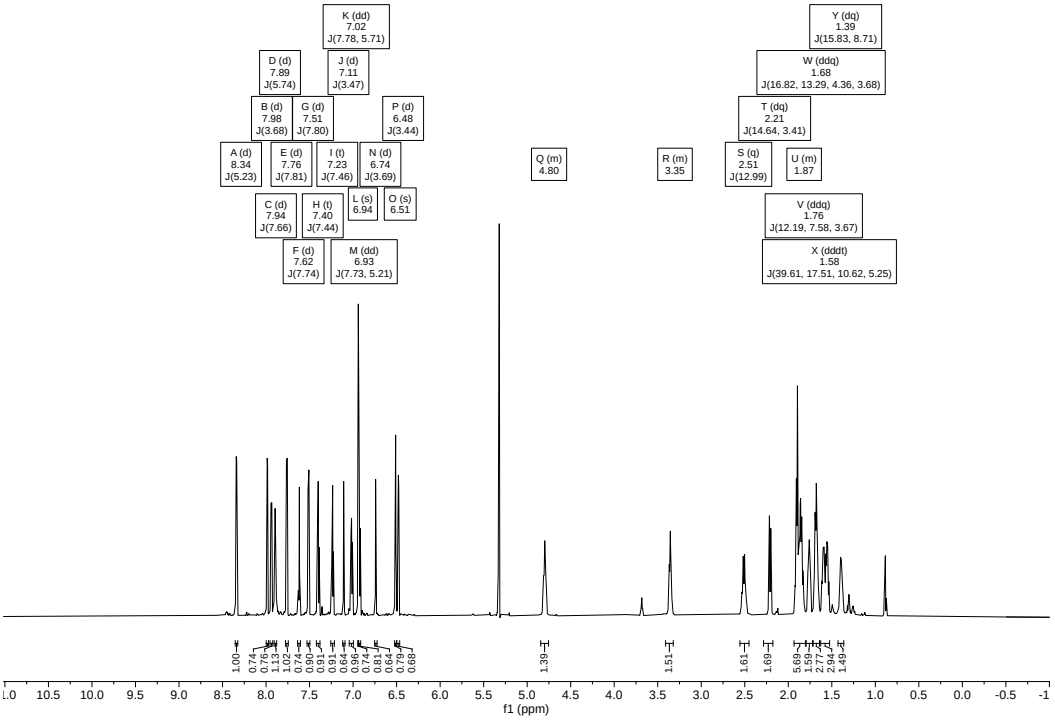

Figure S29. ^{1}H NMR spectrum of (5-^{NP}FP)Ir(COE)Cl (**2f**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm.

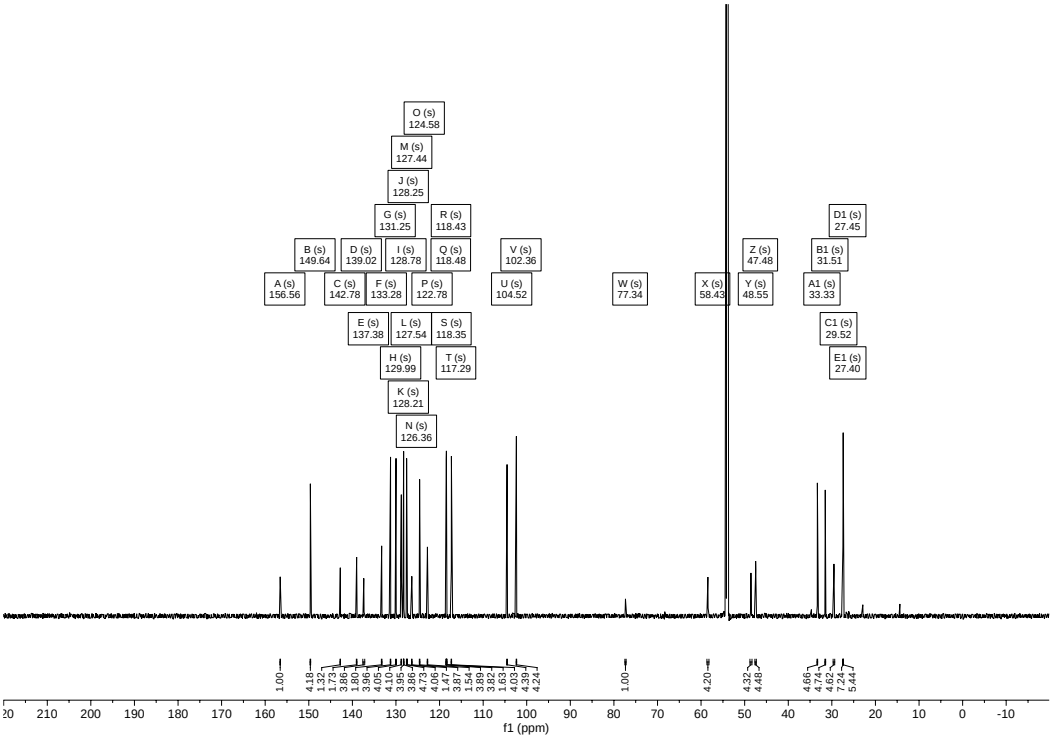

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of (5-^{NP}FP)Ir(COE)Cl (**2f**) in CD_2Cl_2. Minor *n*-pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

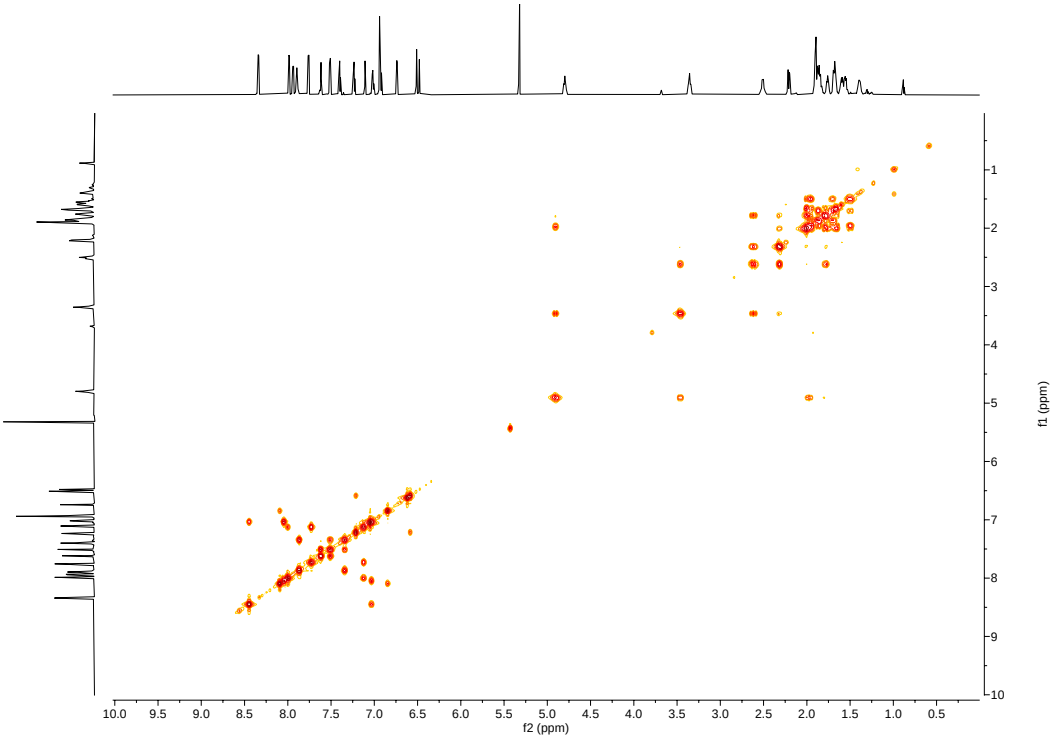

Figure S31. COSY spectrum of (5-^{NP}FP)Ir(COE)Cl (**2f**) in CD_2Cl_2.

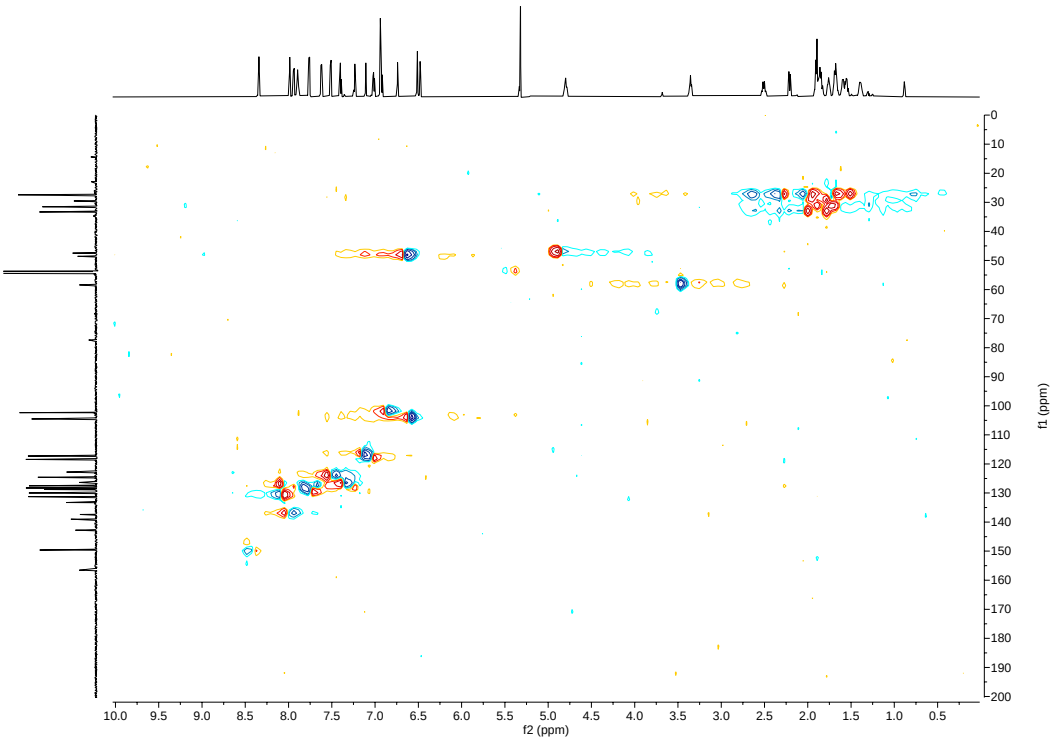

Figure S32. HSQC spectrum of (5-^{NP}FP)Ir(COE)Cl (**2f**) in CD_2Cl_2.

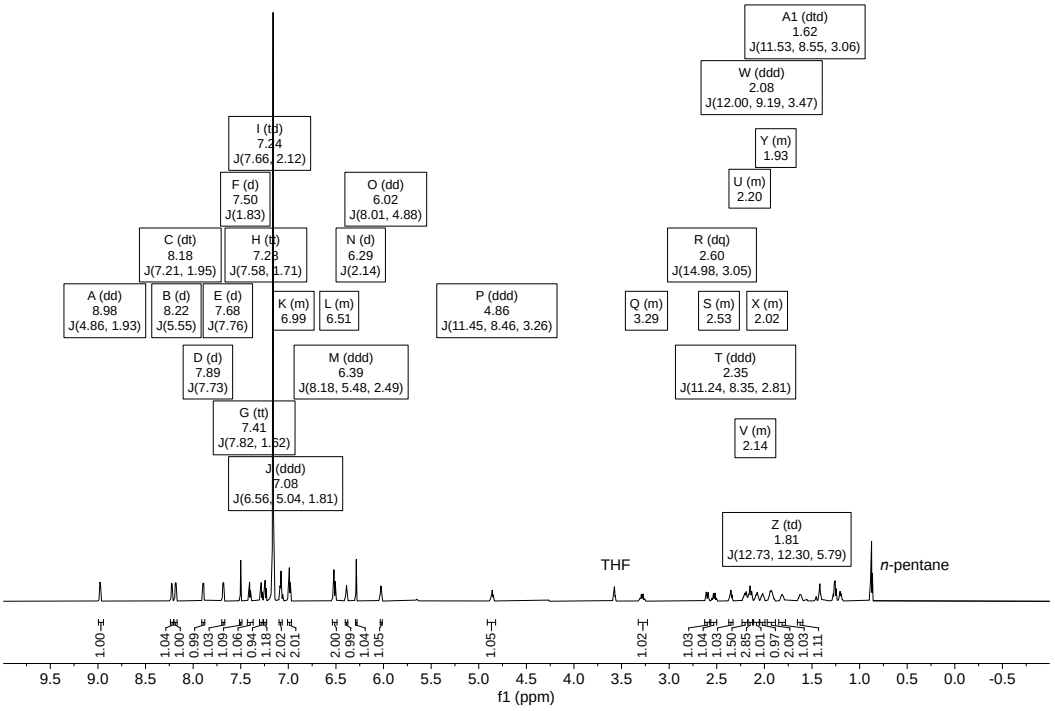

Figure S33. ^{1}H NMR spectrum of (6-^{NP}FP)Ir(COE)Cl (**5f**) in C_6D_6. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm.

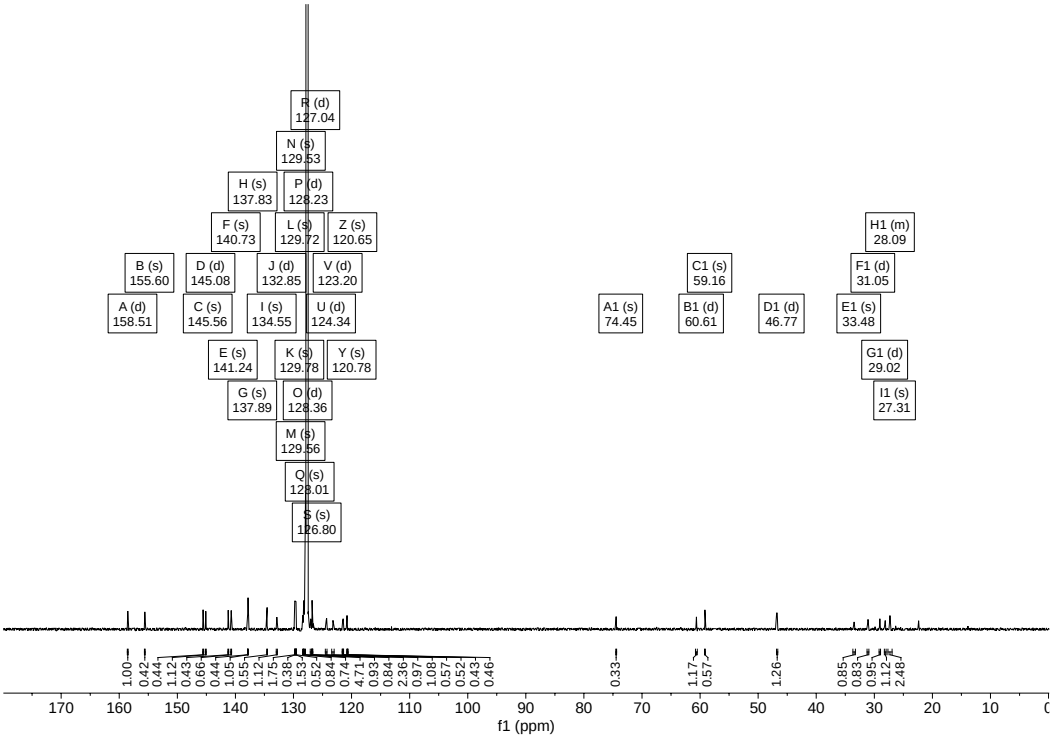

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of (6-^{NP}FP)Ir(COE)Cl (**5f**) C_6D_6.

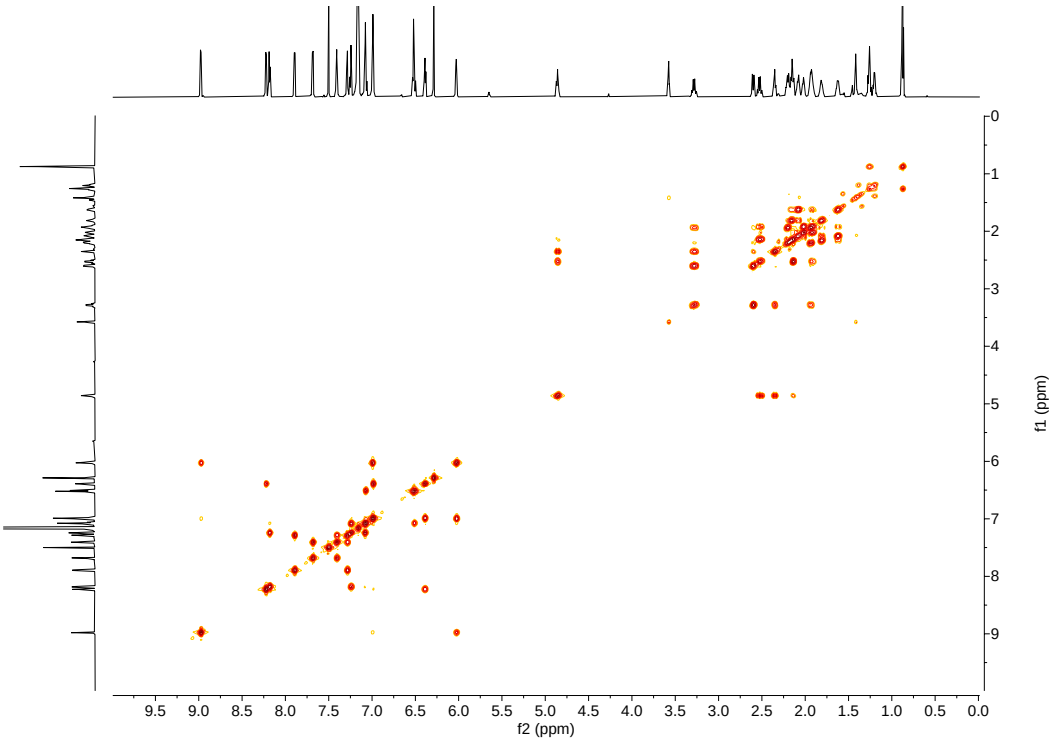

Figure S35. COSY spectrum of (6-^{NP}FP)Ir(COE)Cl (**5f**) C_6D_6.

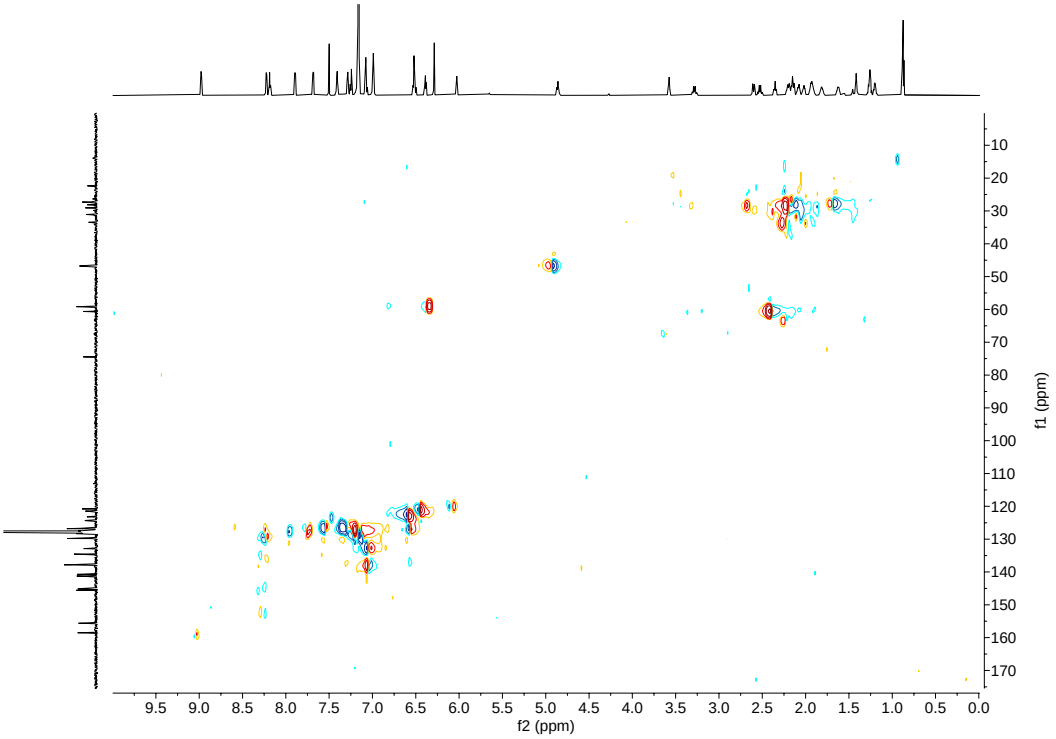

Figure S36. HSQC spectrum of (6-^{NP}FP)Ir(COE)Cl (**5f**) in C_6D_6.

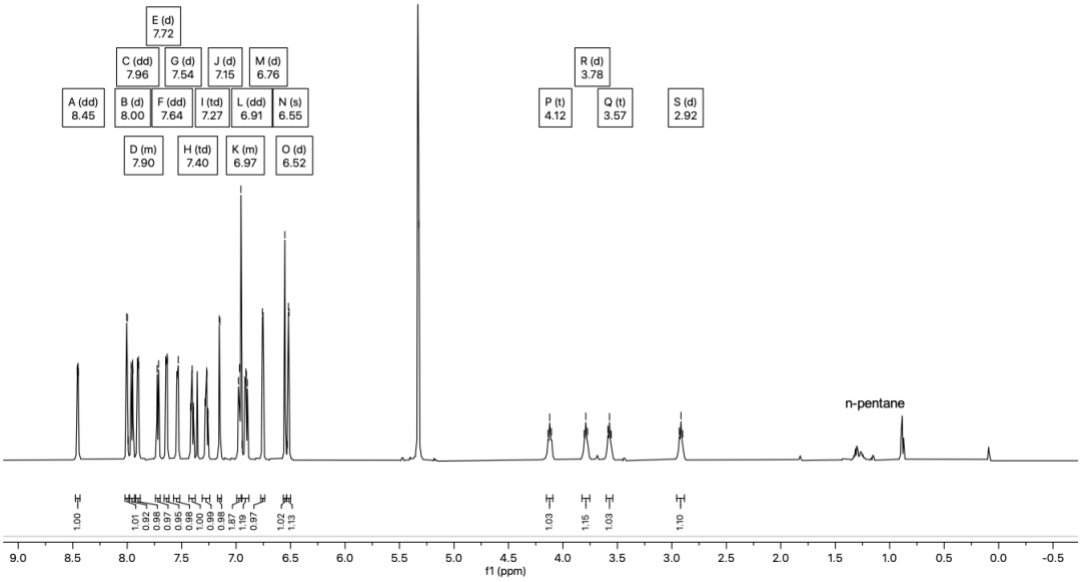

Figure S37. ^{1}H NMR spectrum of (5-^{NP}FP)Ir(C_2H_4)Cl (**2h**) in CD_2Cl_2.

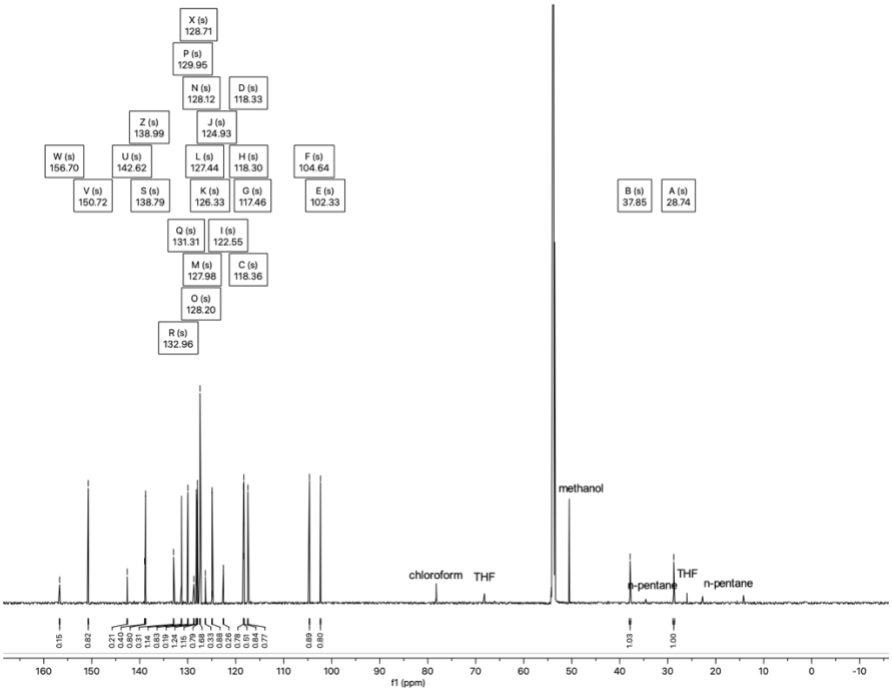

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of (5-^{NP}FP)Ir(C_2H_4)Cl (**2h**) in CD_2Cl_2.

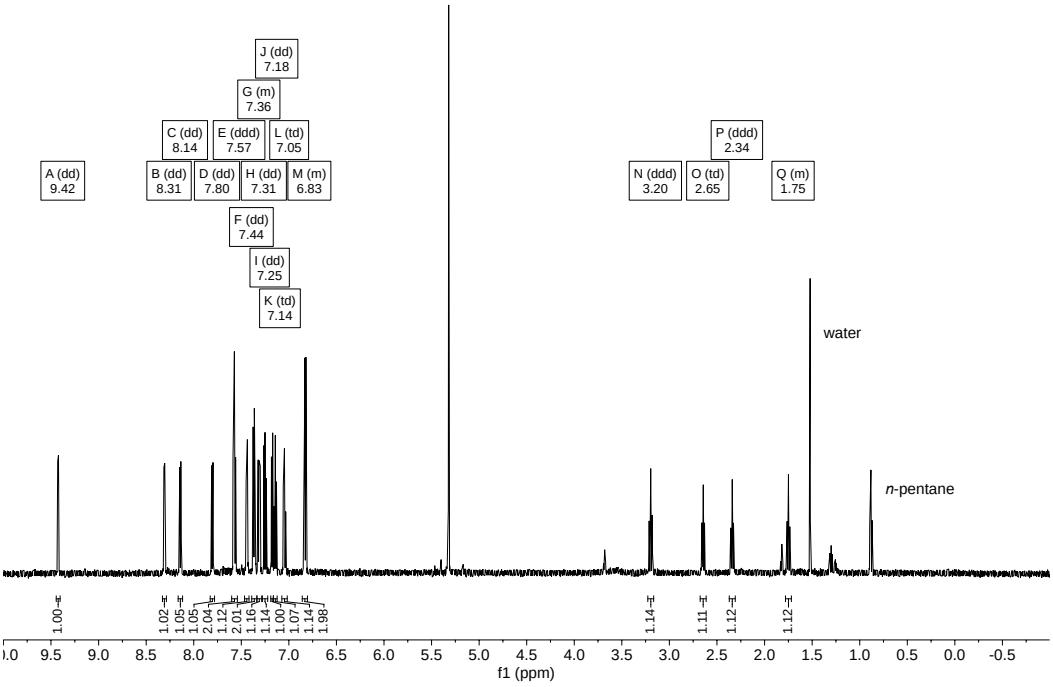

Figure S39. ^{1}H NMR spectrum of (6-FP)Ir(C_2H_4)Cl (**4h**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm along with THF (~3.6 ppm and 1.8 ppm) and water.

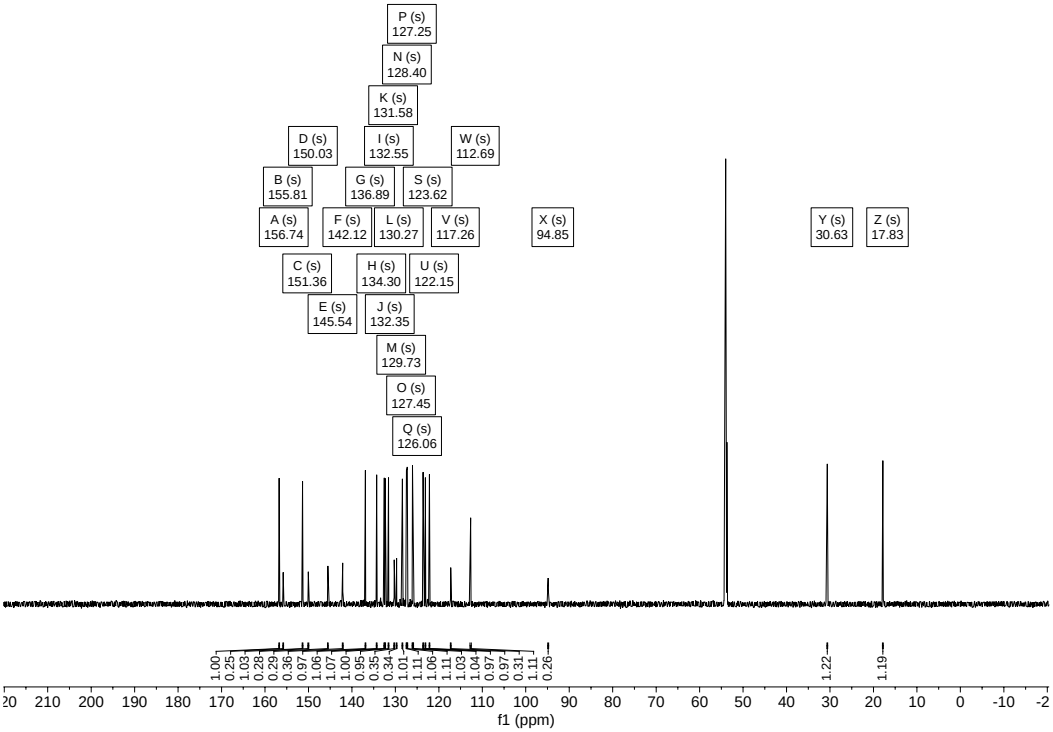

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of (6-FP)Ir(C_2H_4)Cl (**4h**) in CD_2Cl_2.

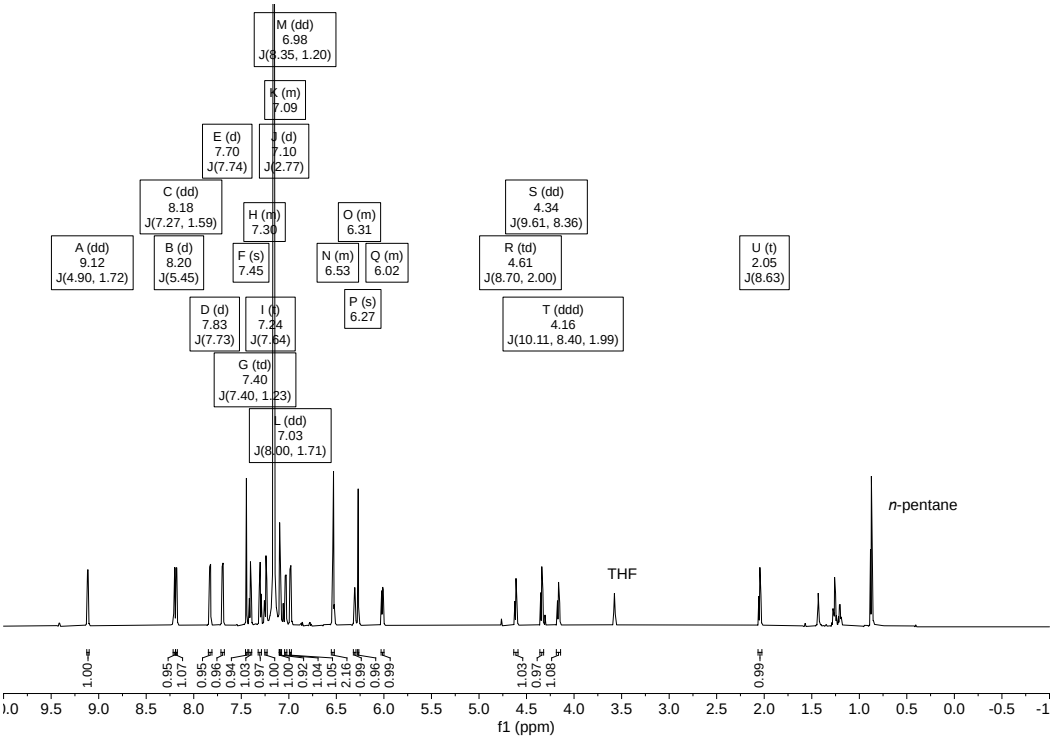

Figure S41. ^{1}H NMR spectrum of (6-^{NP}FP)Ir(C_2H_4)Cl (**5h**) in C_6D_6. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm along with residual THF at ~3.6 ppm and 2.0 ppm.

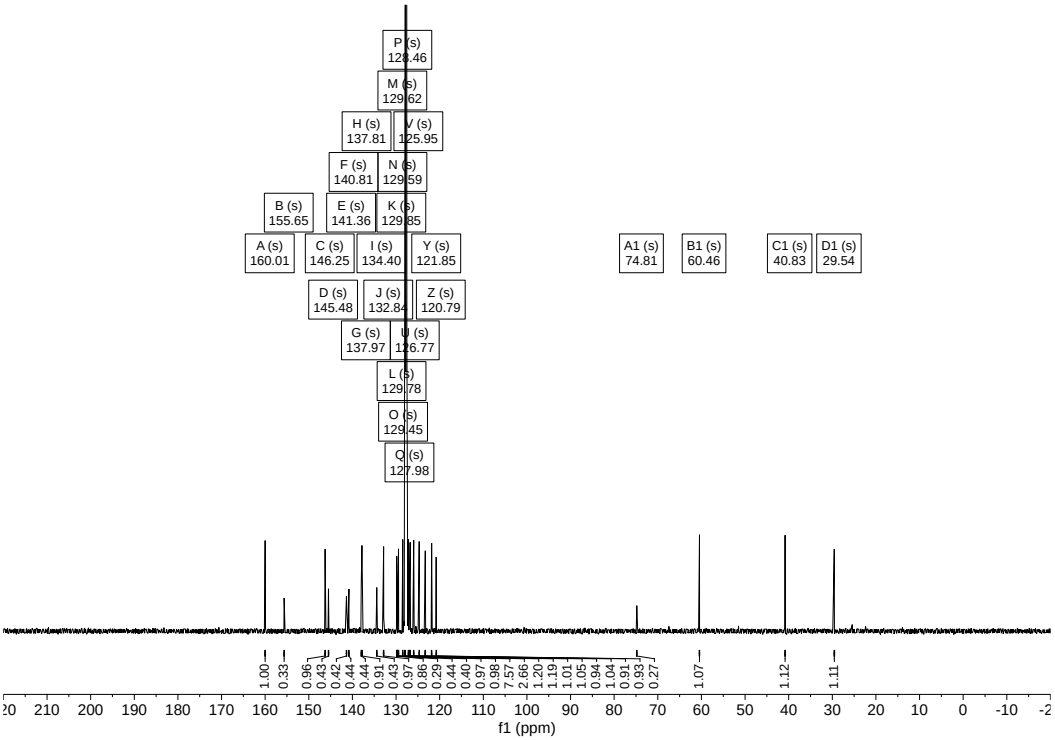

Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of (6-^{NP}FP)Ir(C_2H_4)Cl (**5h**) in C_6D_6.

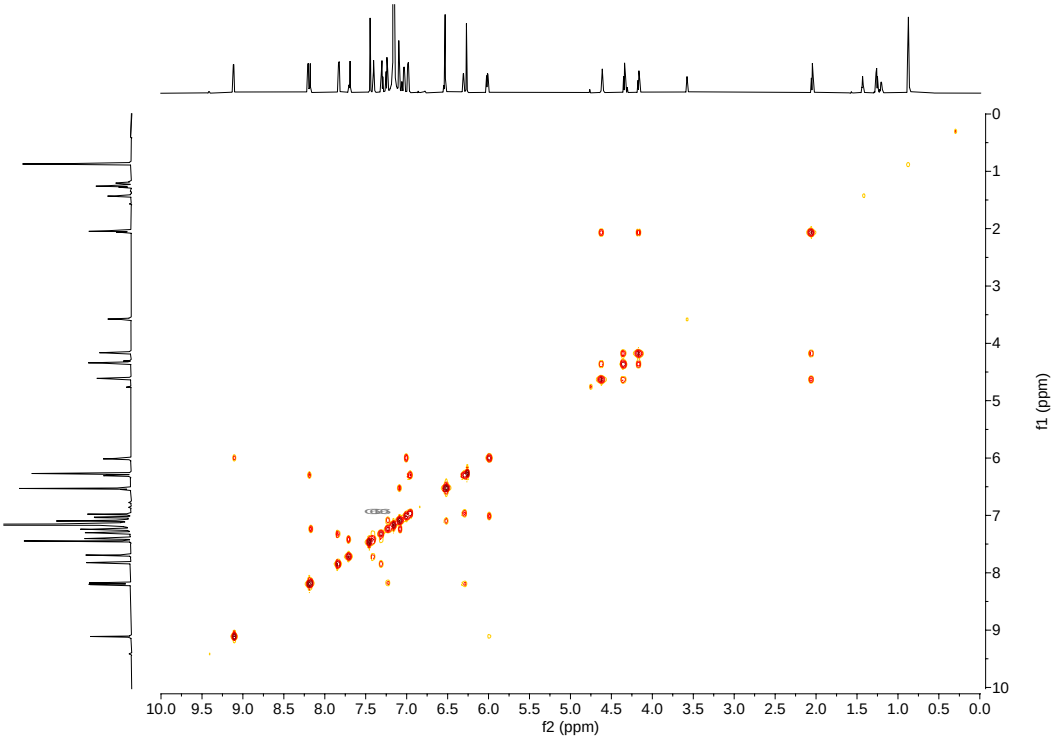

Figure S43. COSY spectrum of (6-^{NP}FP)Ir(C_2H_4)Cl (**5h**) in C_6D_6.

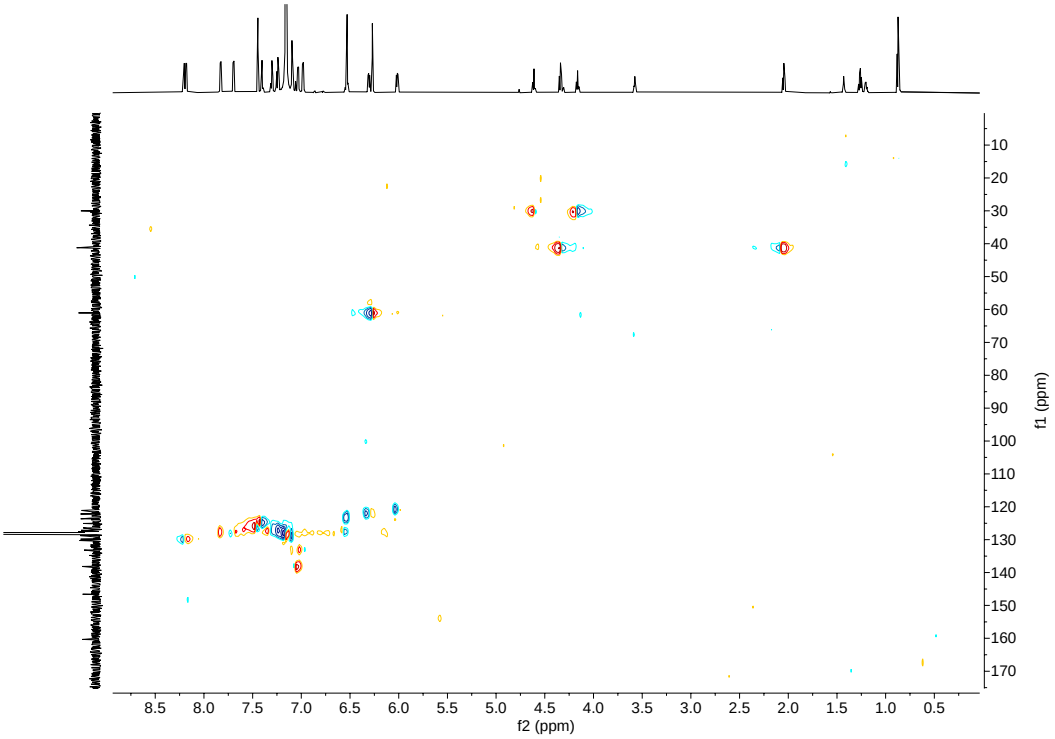

Figure S44. HSQC spectrum of (6-^{NP}FP)Ir(C_2H_4)Cl (**5h**) in C_6D_6.

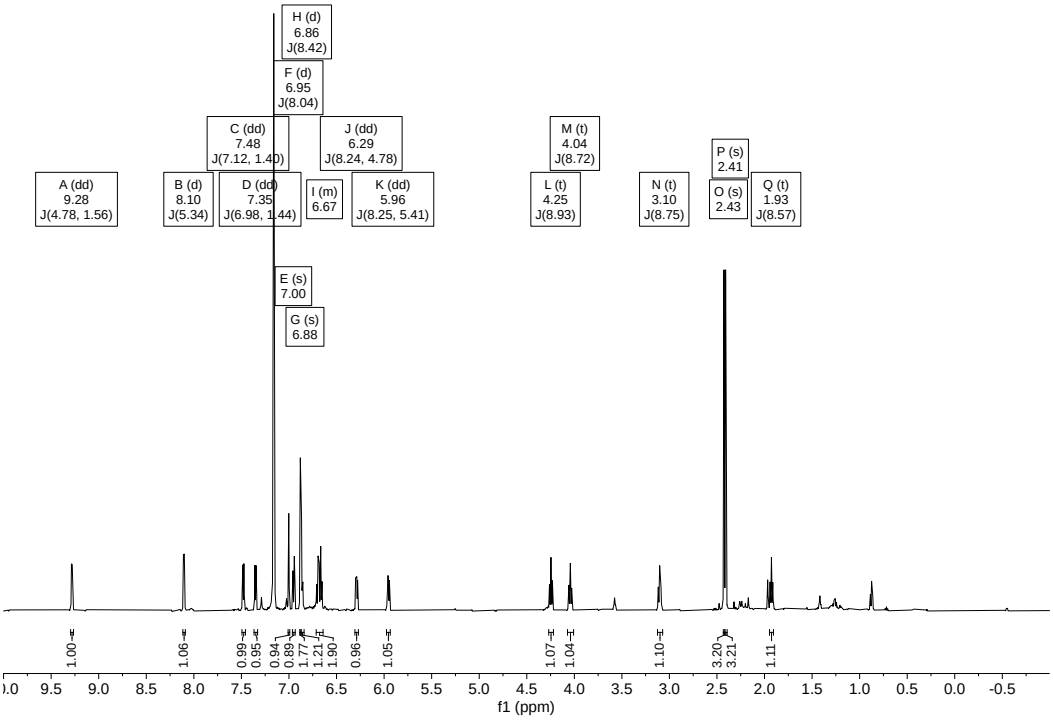

Figure S45. ^{1}H NMR spectrum of (6-^{Me}FP)Ir(C_2H_4)Cl (**6h**) in C_6D_6. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm.

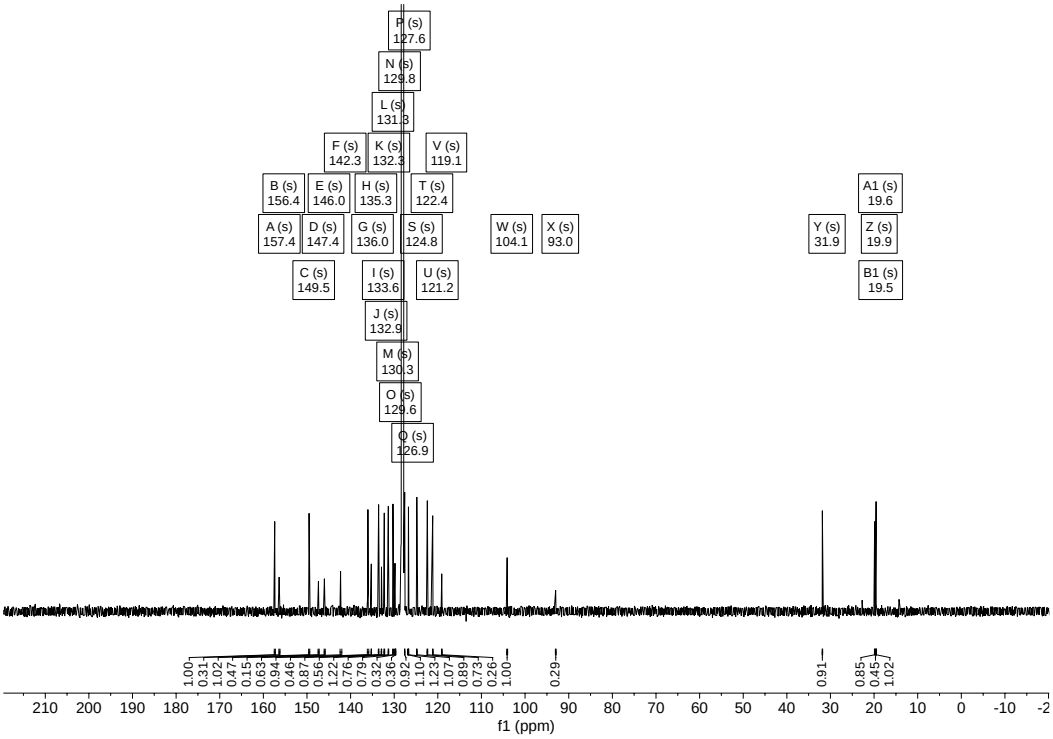

Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of (6-^{Me}FP)Ir(C_2H_4)Cl (**6h**) in C_6D_6. Minor *n*-pentane impurity was observed at 14.2, 22.7 and 34.4 ppm.

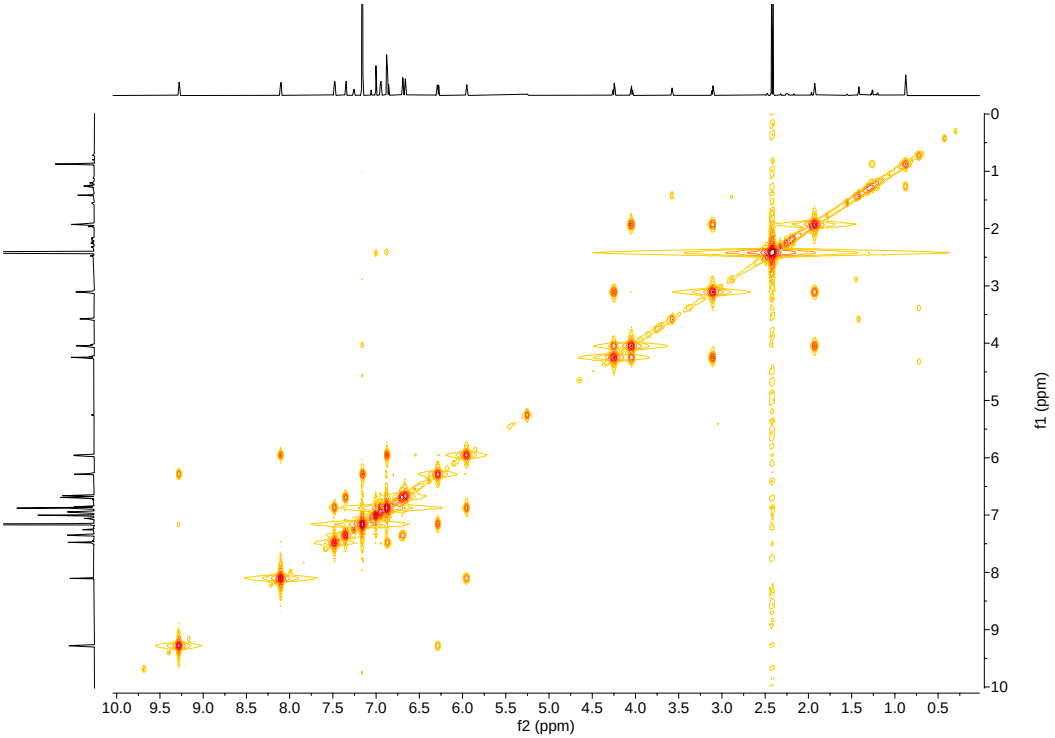

Figure S47. COSY spectrum of (6-^{Me}FP)Ir(C_2H_4)Cl (**6h**) in C_6D_6.

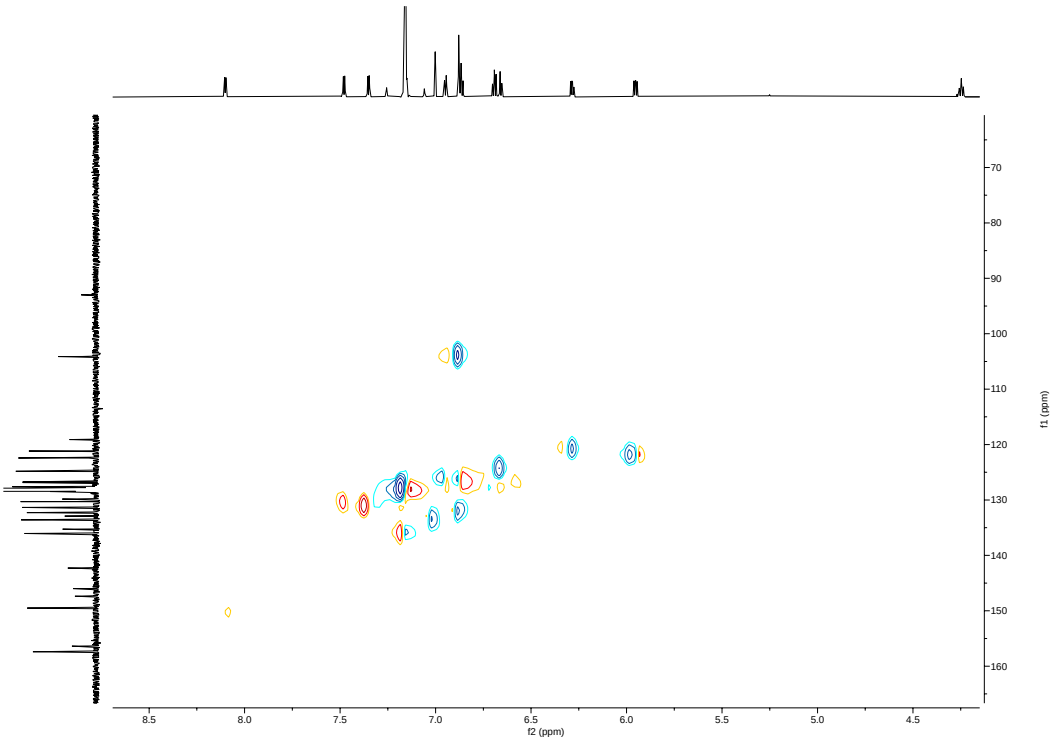

Figure S48. HSQC spectrum of (6-^{Me}FP)Ir(C_2H_4)Cl (**6h**) in C_6D_6.

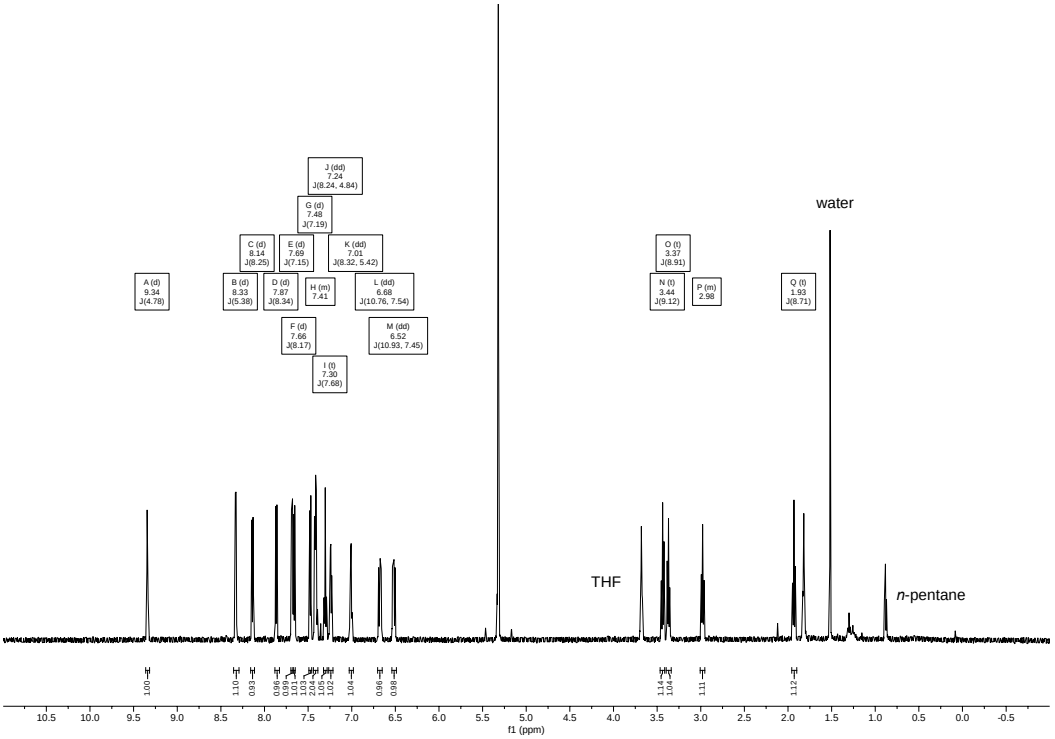

Figure S49. ^{1}H NMR spectrum of (6-^{F}FP)Ir(C_2H_4)Cl (**7h**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm along with residual THF at ~3.6 ppm and 2.0 ppm and water at ~1.5 ppm.

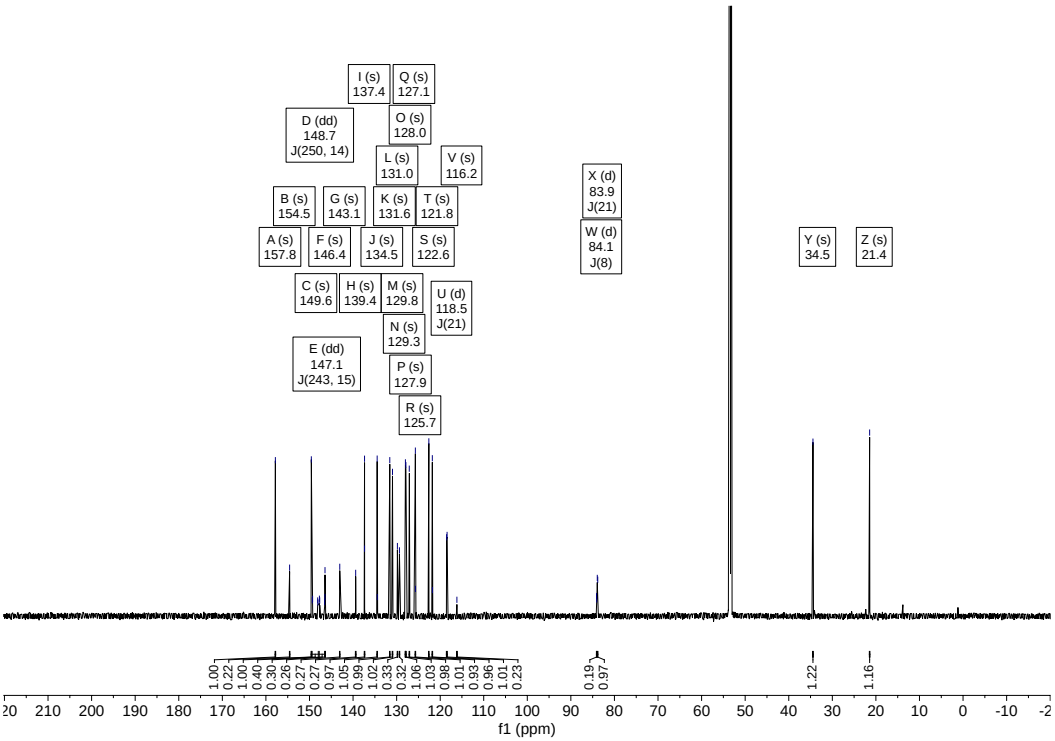

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of (6-^{F}FP)Ir(C_2H_4)Cl (**7h**) in CD_2Cl_2. Minor *n*-pentane impurity was observed at 14.2, 22.8 and 34.6 ppm.

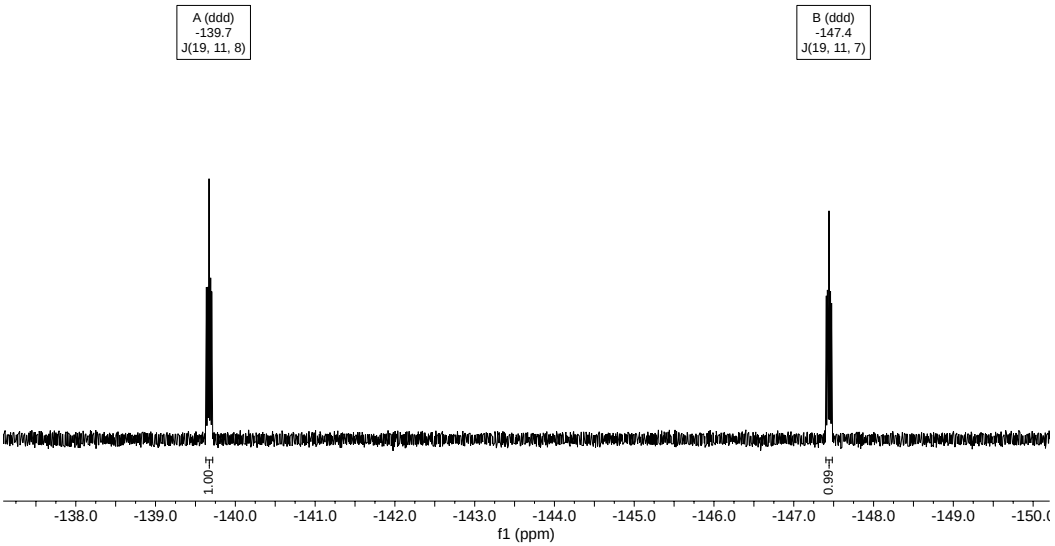

Figure S51. ^{19}F NMR spectrum of (6-^{F}FP)Ir(C_2H_4)Cl (**7h**) in CD_2Cl_2.

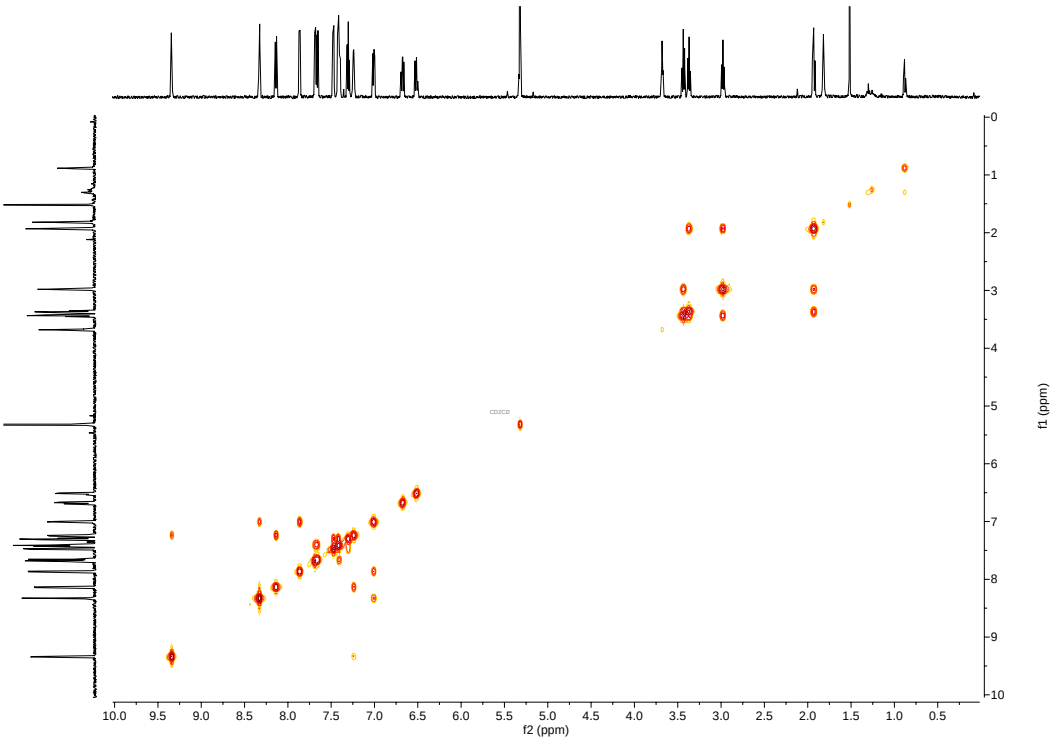

Figure S52. COSY spectrum of (6-^{F}FP)Ir(C_2H_4)Cl (**7h**) in CD_2Cl_2.

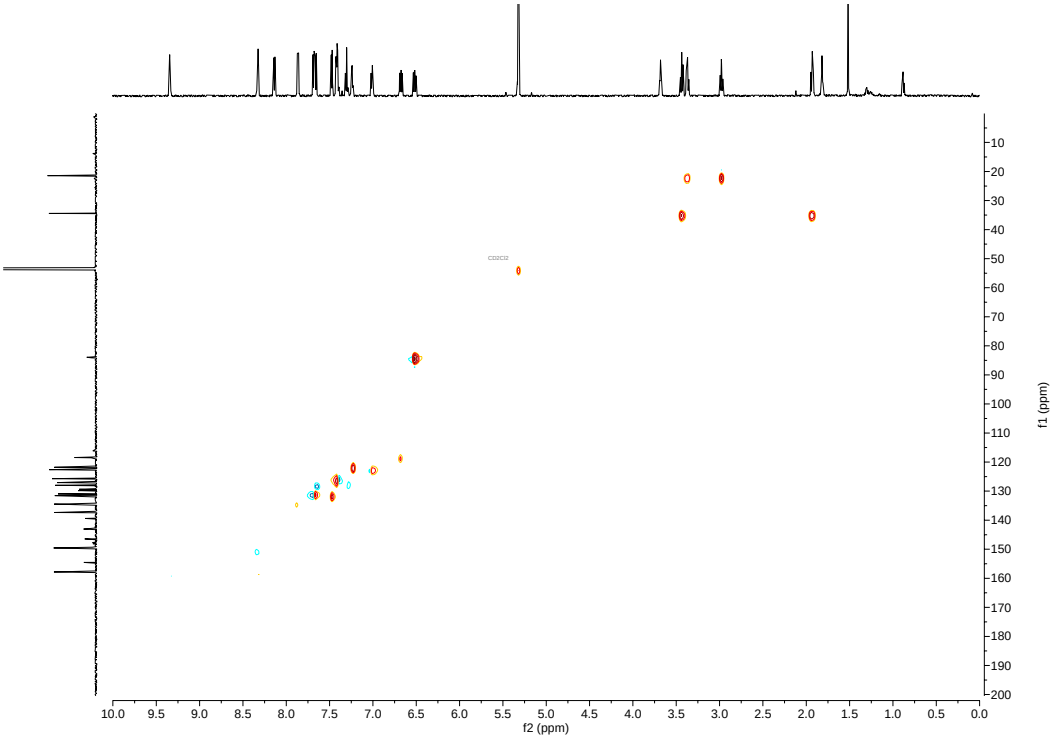

Figure S53. HSQC spectrum of (6-^{F}FP)Ir(C_2H_4)Cl (**7h**) in CD_2Cl_2.

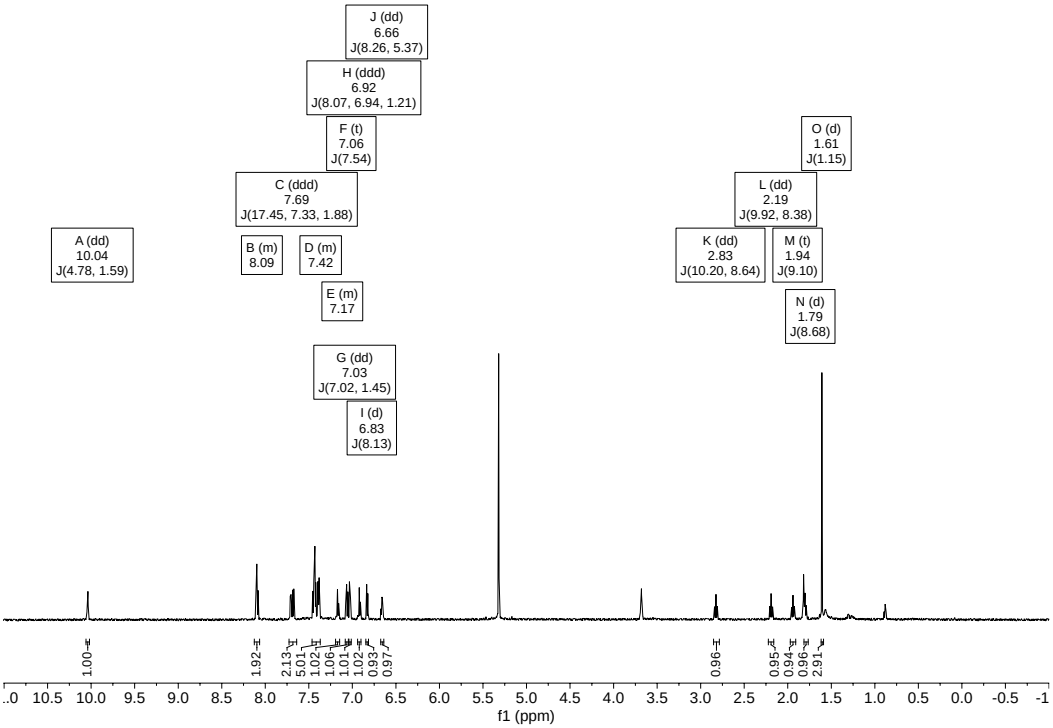

Figure S54. ^{1}H NMR spectrum of (6-FP)Ir(C_2H_4)(OAc) (**4i**) in CD_2Cl_2. Minor THF impurity was observed at ~3.6 ppm and 1.8 ppm.

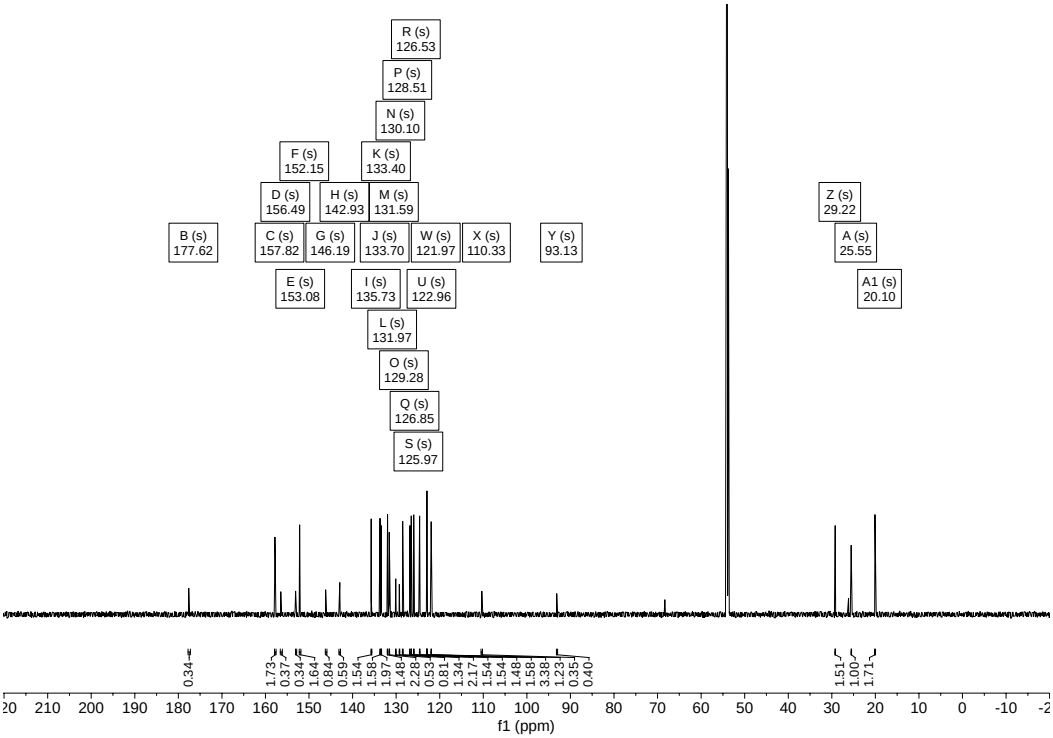

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of (6-FP)Ir(C_2H_4)(OAc) (**4i**) in CD_2Cl_2.

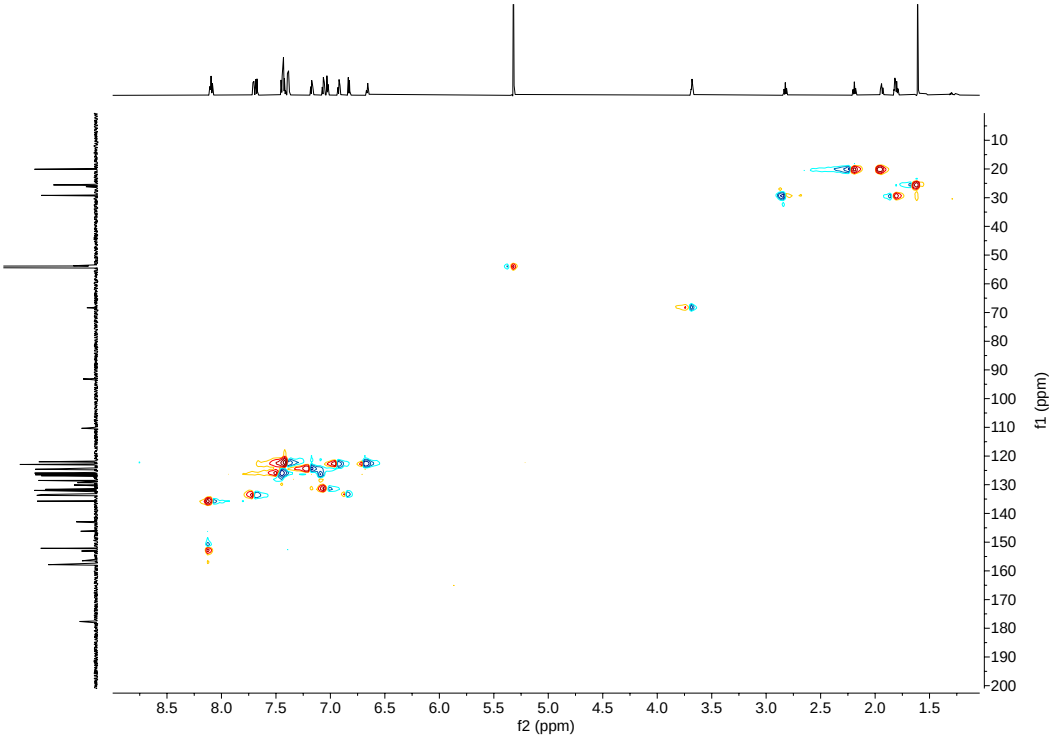

Figure S56. HSQC spectrum of (6-FP)Ir(C_2H_4)(OAc) (**4i**) in CD_2Cl_2.

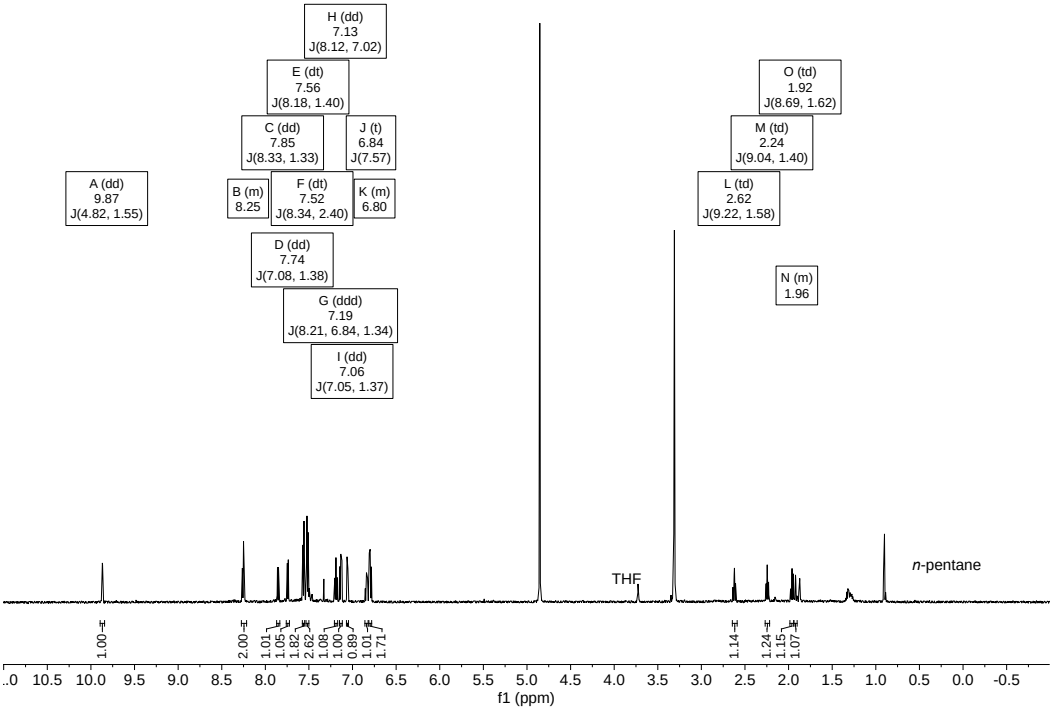

Figure S57. ^{1}H NMR spectrum of (6-FP)Ir(C_2H_4)(TFA) (**4j**) in CD_2Cl_2. Minor *n*-pentane impurity was observed between 0.9 and 1.2 ppm along with residual THF at ~3.6 ppm and 2.0 ppm.

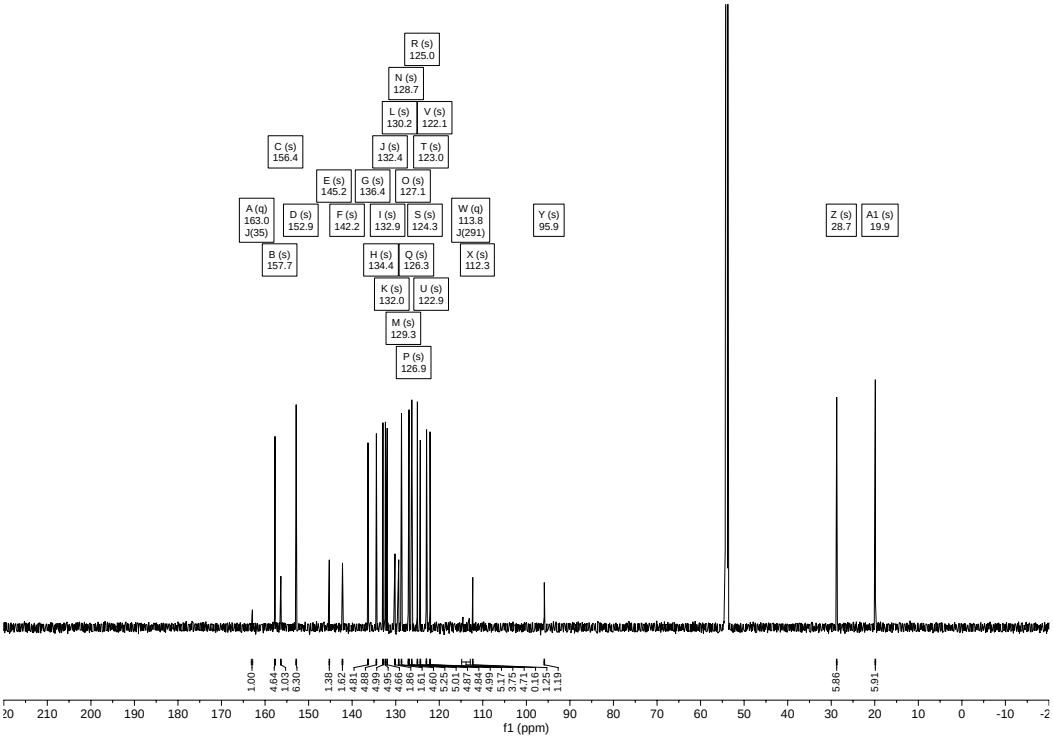

Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of (6-FP)Ir(C_2H_4)(TFA) (**4j**) in CD_2Cl_2.

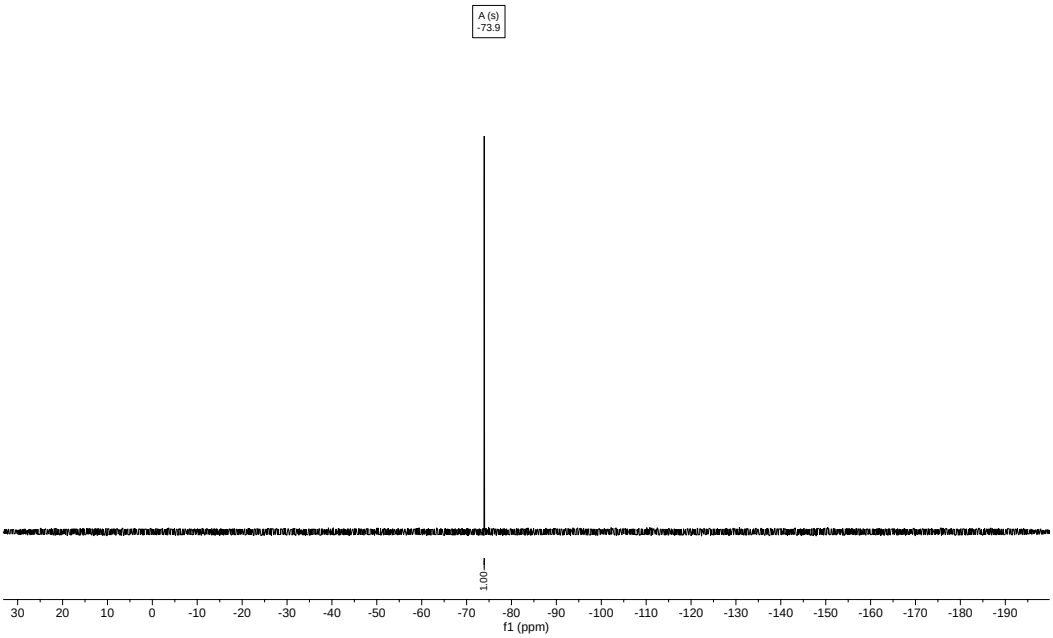

Figure S59. ^{19}F NMR spectrum of (6-FP)Ir(C_2H_4)(TFA) (**4j**) in CD_2Cl_2.

2. ^{1}H NMR Spectra of Selected Complexes at -60 °C

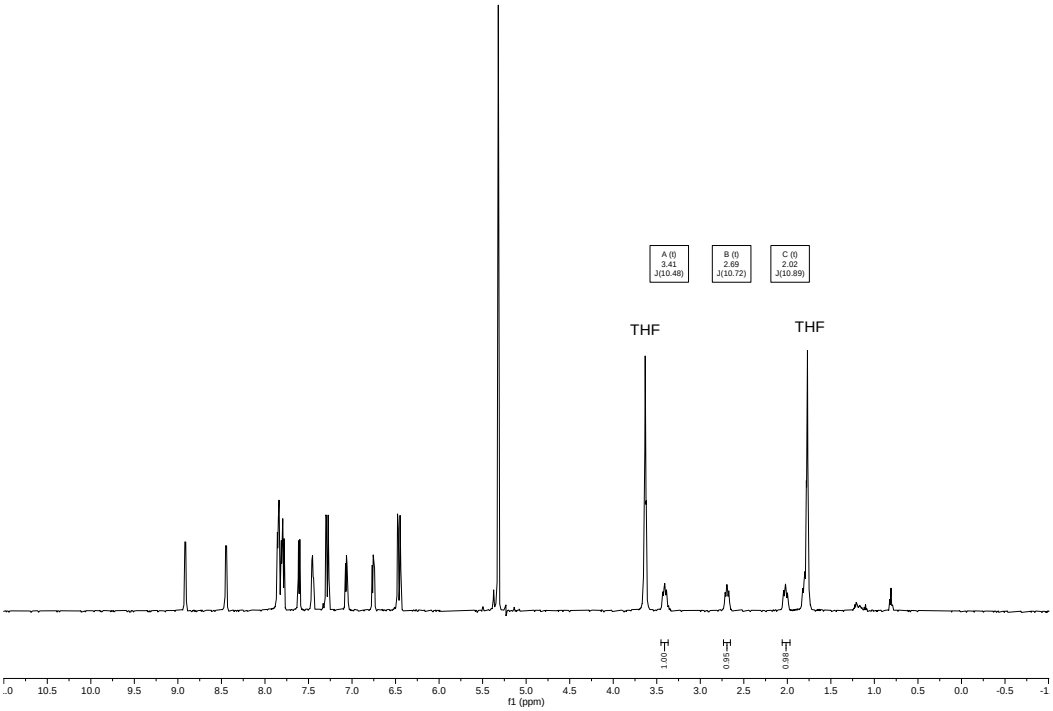

Figure S60. ^{1}H NMR spectrum of (5-FP)Rh(C_2H_4)Cl (**1a**) in CD_2Cl_2 at -60 °C. The fourth ethylene peak is overlapped with THF residue (~3.6 and 1.8 ppm), which was co-crystalized with (5-FP)Rh(C_2H_4)Cl.

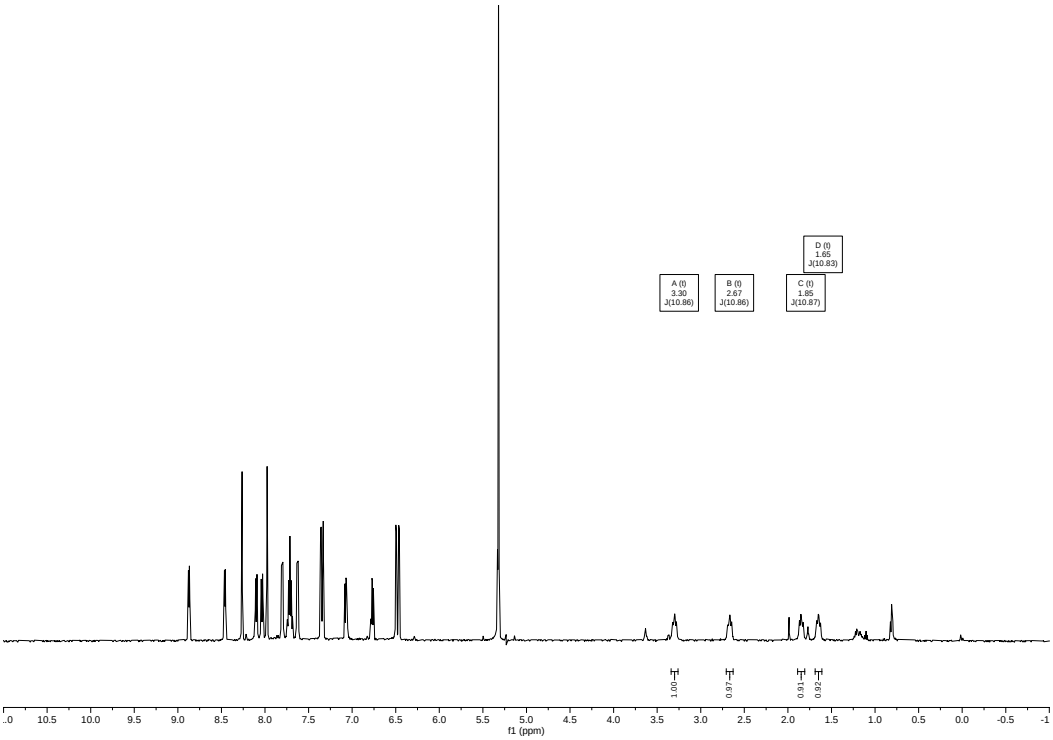

Figure S61. ^{1}H NMR spectrum of (5-^{NP}FP)Rh(C_2H_4)Cl (**2a**) in CD_2Cl_2 at -60 °C.

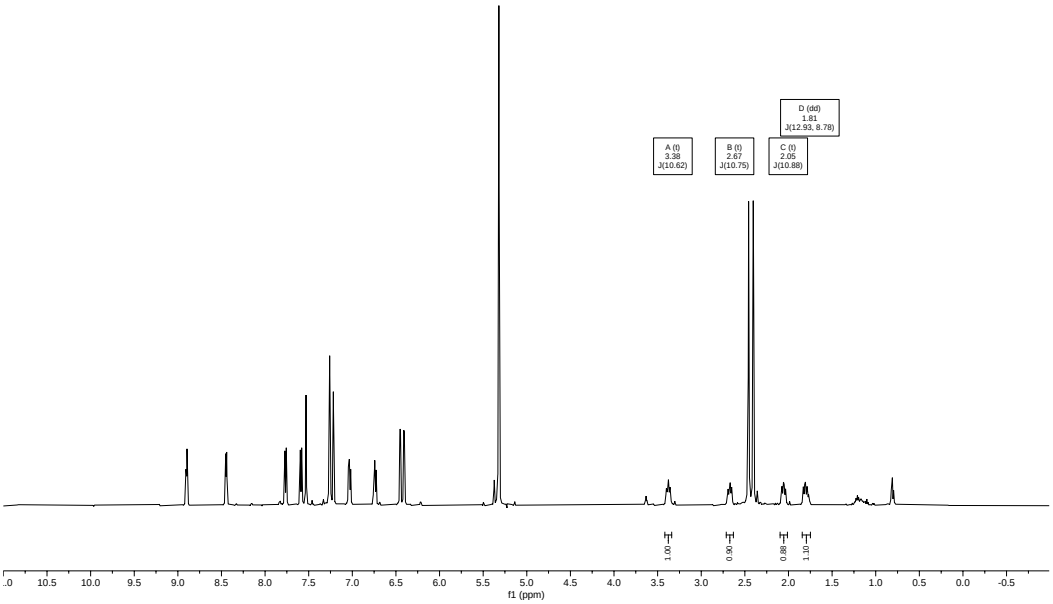

Figure S62. ^{1}H NMR spectrum of (5-^{Me}FP)Rh(C_2H_4)Cl (**3a**) in CD_2Cl_2 at -60 °C.

3. Formation of cyclooctane in the synthesis of [(5-FP)Ir(COD)][IrCl$_2$(COD)].

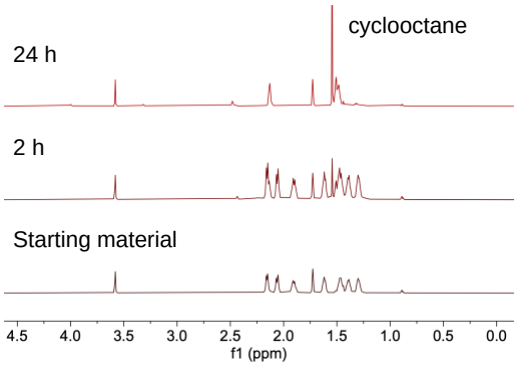

Figure S63. Cyclooctane peak growing in ^{1}H NMR spectra during the synthesis of [(5-FP)Ir(η^2,η^2-COD)][IrCl$_2$(η^2,η^2-COD)] (**1b**) in THF-d_8.

4. Variable Temperature NMR Experiments to determine rotational barriers of coordinated ethylene

4.1 Examples of NMR spectra of coordinated ethylene at different temperatures

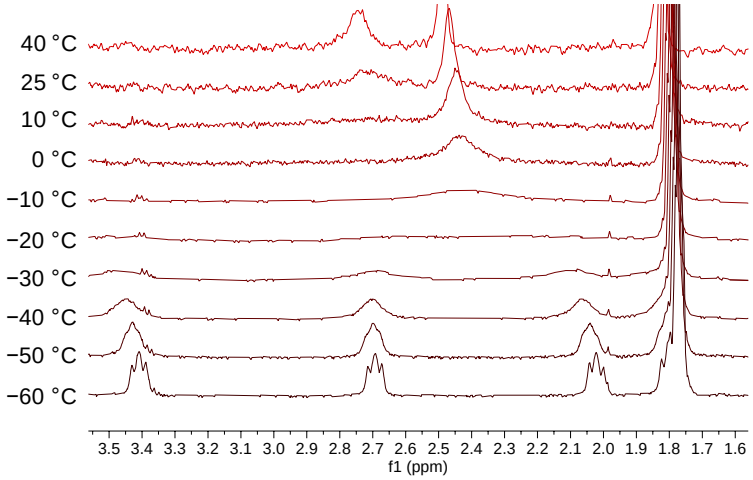

Figure S64. Stacked ^{1}H NMR spectra of (5-FP)Rh(C_2H_4)Cl (**1a**) in CD_2Cl_2 at different temperatures (one proton of the ethylene is overlapped with THF solvent residue).

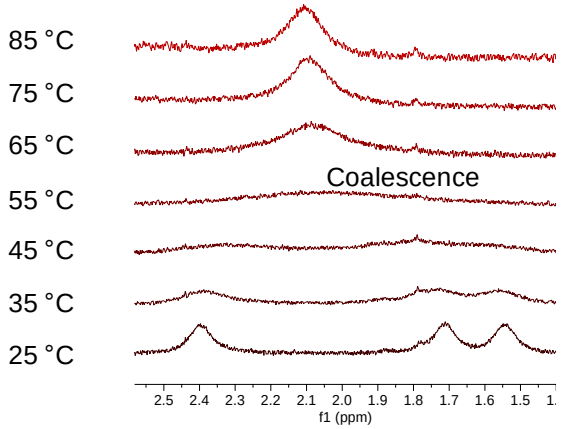

Figure S65. Stacked ^{1}H NMR spectra of (6-FP)Rh(C_2H_4)Cl (**4a**) in DMF-d_7 at different temperatures (one resonance for ethylene is outside the region depicted).

4.2 Eyring plots for ethylene rotational barriers

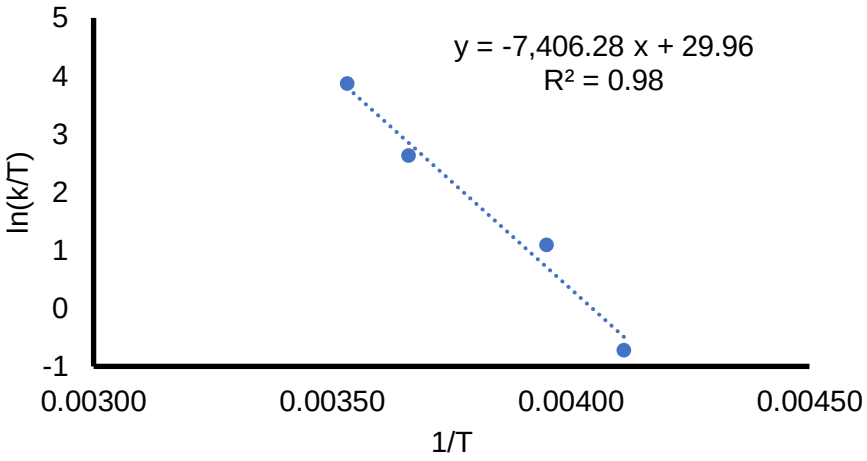

Figure S66. Eyring plot for ethylene rotational barrier of (5-FP)Rh(C_2H_4)Cl (**1a**).

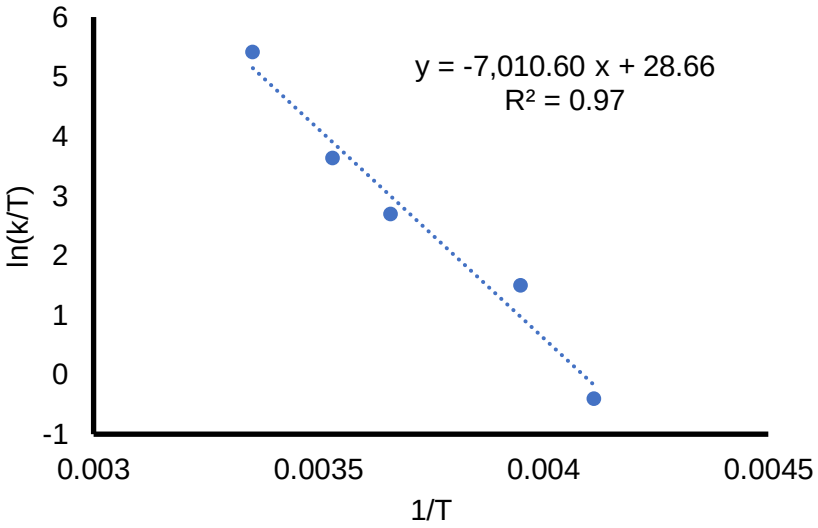

Figure S67. Eyring plot for ethylene rotational barrier of (5-^{NP}FP)Rh(C_2H_4)Cl (**2a**).

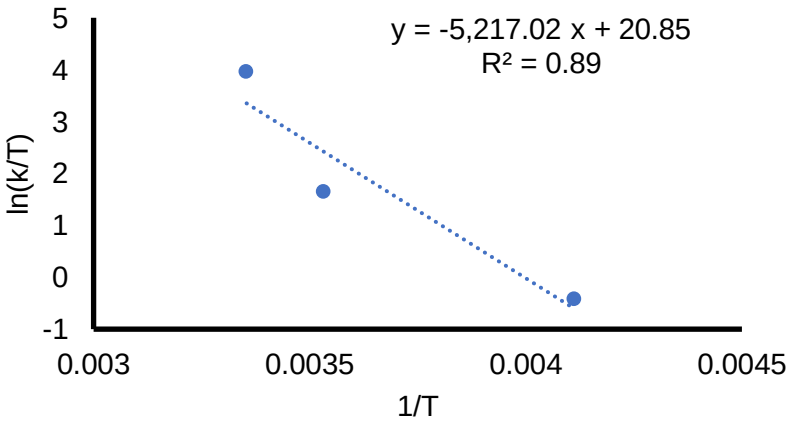

Figure S68. Eyring plot for ethylene rotational barrier of (5-^{Me}FP)Rh(C_2H_4)Cl (**3a**).

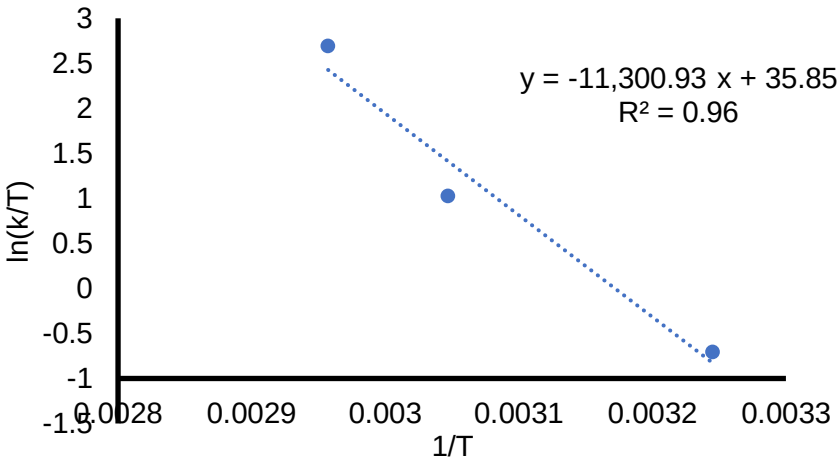

Figure S69. Eyring plot for ethylene rotational barrier of (6-FP)Rh(C_2H_4)Cl (**4a**).

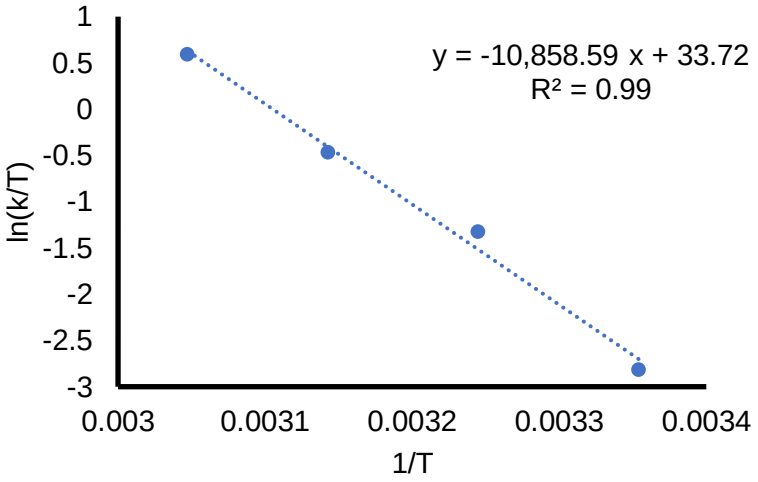

Figure S70. Eyring plot for ethylene rotational barrier of (6-^{Me}FP)Rh(C_2H_4)Cl (**6a**).

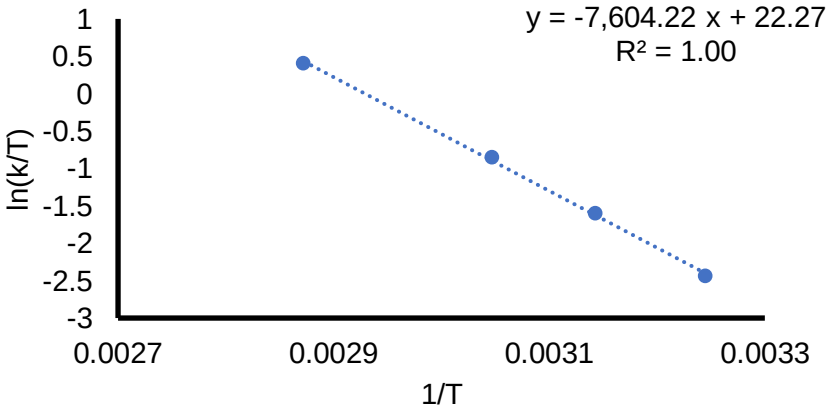

Figure S71. Eyring plot for ethylene rotational barrier of (5-^{NP}FP)Ir(C_2H_4)Cl (**2h**).

5. Crystal Structure Data

Crystallographic details: A suitable single crystal of each sample was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system. An Incoatec Microfocus IμS (Cu K_α, λ = 1.54178 Å) and a multi-layer mirror monochromator were used for **1c, 3d**. A fine-focus sealed tube (Mo K_α, λ = 0.71073 Å) and a graphite monochromator were used for **3, 6, 6a, 1b, 1e-BF4, 3e-BF4, 5f, 4g, 5g, 7g, 4h, 6h, 7h, 4i. 4j**. The frames were integrated with the Bruker SAINT software package[1] using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS)[11] (or TWINABS for **3e-BF_4**) Each structure was solved and refined using the Bruker SHELXTL Software Package[2] within APEX3[1] and OLEX2.[3] Non-hydrogen atoms were refined anisotropically. The O-H hydrogen atom in **7g** and the ethylene hydrogen atoms in **4i** were located in the electron density map and refined isotropically. All other hydrogen atoms in all structures were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (1.5U_{equiv} for methyl).

For **1b**, the cation was disordered over two positions, but since the minor component refined to less than two percent occupancy, only the iridium position was modeled. For **1e-BF_4**, the symmetry-disordered THF molecule was refined at half-occupancy with constraints on the anisotropic displacement parameters of its C atoms, and restraints on its bond lengths. Due to the very weak diffraction of **3d**, the data were truncated at a resolution of 0.95 Å and a global RIGU restraint was used on the structure. The relative occupancy of the disordered atoms in one anion was freely refined, with restraints on the bond lengths and anisotropic displacement parameters of the disordered atoms. A two-domain twin was identified for **3e-BF_4**. Starting with 2551 reflections, CELL_NOW[4] fit 2035 reflections to the first domain, 1534 to the second domain (513 exclusively), with 3 unindexed reflection remaining. The twin domain was oriented at a 2.6° rotation about the reciprocal axis 0.215 1.000 0.009. The twin law was 0.999 0.002 -0.094 / -0.001 1.000 0.005 / 0.023 -0.001 0.999. The structure was refined on HKLF5 data, with the BASF for the twin domains refining to 0.32423. In **5f**, a mixture of THF, pentane and benzene solvent located in the crystal lattice was severely disordered and could not be adequately modeled with or without restraints. Thus, the structure factors were modified using the PLATON SQUEEZE[5] technique, in order to produce a “solvate-free” structure factor set. PLATON reported a total electron density of 154 e^- and total solvent accessible volume of 734 $Å^3$. Two carbon atoms in each COE ligand were each disordered over two positions. The relative occupancies of the positions were freely refined, with constraints on the anisotropic displacement parameters of the disordered atoms and restraints on the disordered bonds. In **4g**, the fluorine atoms of the CF_3 group were found to be disordered over two positions. The relative occupancies were freely refined, and constraints or restraints were needed. In **5g**, one of the two solvent sites was found to be a severely disordered mixtures of benzene and THF that could not be adequately modeled with or without restraints. Thus, the structure factors were modified using the PLATON SQUEEZE[5] technique, in order to produce a “solvate-free” structure factor set. PLATON reported a total electron density of 79 e^- and total solvent accessible volume of 445 $Å^3$. In **7g**, the CF_3 group and part of the cyclooctene group were each disordered over two positions. The relative occupancies were freely refined, and constraints were used on the anisotropic displacement parameters of some of the disordered atoms. In **4j**, the fluorine atoms of the CF_3 group were disordered over two positions. The relative occupancies of the major and minor site were freely

refined, and constraints were used on the anisotropic displacement parameters of the disordered atoms.

Table S1. Crystal data for **3**, **6**, **and 6a**.

	3	**6**	**6a**
Chemical formula	$C_{22}H_{18}N_4$	$C_{26}H_{20}N_2$	$C_{28}H_{24}ClN_2Rh$
FW (g/mol)	338.40	360.44	526.85
T (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	0.252 x 0.288 x 0.398	0.142 x 0.205 x 0.212	0.029 x 0.040 x 0.325
Crystal habit	colorless block	colorless rod	orange rod
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	P $2_1/c$	P b c a	P $2_12_12_1$
a (Å)	9.7670(15)	13.5183(13)	10.9057(14)
b (Å)	17.682(3)	16.7398(17)	11.3576(14)
c (Å)	10.6205(16)	16.9247(17)	18.834(3)
α (°)	90	90	90
β (°)	111.111(4)	90	90
γ (°)	90	90	90
V ($Å^3$)	1711.1(4)	3830.0(7)	2332.8(5)
Z	4	8	4
ρ_{calc} ($g/cm^{3)}$	1.314	1.250	1.500
μ (mm^{-1})	0.080	0.073	0.865
F(000)	712	1520	1072
θ range (°)	2.23 to 29.56	2.28 to 27.12	2.09 to 25.73
Index ranges	-13 ⩽ h ⩽ 13 -19 ⩽ k ⩽ 24 -14 ⩽ l ⩽ 14	-17 ⩽ h ⩽ 17 -21 ⩽ k ⩽ 21 -21 ⩽ l ⩽ 21	-13 ⩽ h ⩽ 13 -13 ⩽ k ⩽ 12 -22 ⩽ l ⩽ 22
Reflns coll.	21470	34540	22992
Ind. reflns	4800 [R_{int} = 0.0273]	4229 [R_{int} = 0.0672]	4437 [R_{int} = 0.1404]
Data / restraints / parameters	4800 / 0 / 237	4229 / 0 / 255	4437 / 0 / 291
Goodness-of-fit on F^2	1.027	0.929	1.032
R_1 [I>2σ(I)]	0.0406	0.0427	0.0594
wR_2 [all data]	0.1110	0.1389	0.1321

Table S2. Crystal data for **1b**, **1c**, **1e-BF_4**, **3d** and **3e-BF_4**.

	1b	**1c**	**1e-BF_4**	**3d**	**3e-BF_4**
Chemical formula	$C_{36}H_{38}Cl_2Ir_2N_4$	$C_{40}H_{38}F_6Ir_2N_4O_4$	$C_{52}H_{52}B_2F_8Ir_2N_8O$	$C_{30}H_{34}Cl_2Ir_2N_4$	$C_{26}H_{26}BF_4IrN_4$
FW (g/mol)	982.00	1137.14	1363.03	905.91	673.52
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	1.54178	0.71073	1.54178	0.71073
Crystal size (mm)	0.099 x 0.137 x 0.156	0.067 x 0.071 x 0.210	0.056 x 0.094 x 0.133	0.036 x 0.075 x 0.345	0.030 x 0.049 x 0.587
Crystal habit	yellow plate	yellow plate	orange plate	orange needle	orange rod
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal
Space group	P 2_1/n	P c	P 2_1/c	P 2_1/c	I 4_1/a
a (Å)	12.9657(10)	14.1766(4)	9.7465(7)	18.2584(7)	27.223(2)
b (Å)	15.5207(12)	10.4321(3)	12.4829(9)	9.6008(4)	27.223(2)
c (Å)	15.4504(12)	24.9964(8)	20.2685(18)	33.7671(15)	13.3683(15)
α (°)	90	90	90	90	90
β (°)	91.985(2)	95.593(2)	99.382(3)	98.723(3)	90
γ (°)	90	90	90	90	90
V ($Å^3$)	3107.3(4)	3679.16(19)	2433.0(3)	5850.7(4)	9907.1(18)
Z	4	4	2	8	16
ρ_{calc} ($g/cm^{3)}$	2.099	2.053	1.861	2.057	1.806
μ (mm^{-1})	8.763	14.494	5.544	19.237	5.444
F(000)	1880	2184	1328	3440	5248
θ range (°)	1.86 to 29.61	3.13 to 68.38	1.92 to 26.38	2.45 to 54.00	1.50 to 27.11
Index ranges	-18 ⩽ h ⩽ 18 -21 ⩽ k ⩽ 21 -21 ⩽ l ⩽ 21	-17 ⩽ h ⩽ 17 -12 ⩽ k ⩽ 12 -30 ⩽ l ⩽ 30	-12 ⩽ h ⩽ 12 -15 ⩽ k ⩽ 15 -25 ⩽ l ⩽ 25	-19 ⩽ h ⩽ 19 -10 ⩽ k ⩽ 10 -35 ⩽ l ⩽ 35	-24 ⩽ h ⩽ 24 0 ⩽ k ⩽ 34 0 ⩽ l ⩽ 17
Reflns coll.	38068	55898	20549	29231	113893
Ind. reflns	8737 [R_{int} = 0.0657]	13482 [R_{int} = 0.0631]	4973 [R_{int} = 0.0825]	6976 [R_{int} = 0.1012]	5950 [R_{int} = 0.0650
Data / restraints / parameters	8737 / 0 / 401	13482 / 2 / 980	4973 / 4 / 334	6976 / 834 / 753	5950 / 0 / 328
Goodness-of-fit on F^2	1.011	1.014	1.018	1.134	1.029
R_1 [I>2σ(I)]	0.0337	0.0282	0.0414	0.0973	0.0339
wR_2 [all data]	0.0637	0.0664	0.0789	0.2338	0.0730

Table S3. Crystal data for **5f**, **4g**, **5g** and **7g**.

	5f	**4g**	**5g**	**7g**
Chemical formula	$C_{36}H_{32}ClIrN_2$	$C_{34}H_{30}F_3IrN_2O_2$	$C_{234}H_{198}F_{18}Ir_6N_{12}O_{12}$	$C_{38}H_{36}F_5IrN_2O_3$
FW (g/mol)	720.28	747.80	4865.23	855.89
T (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal size (mm)	0.040 x 0.070 x 0.120	0.115 x 0.145 x 0.290	0.087 x 0.105 x 0.152	0.095 x 0.115 x 0.148
Crystal habit	red plate	red plate	red rod	red block
Crystal system	monoclinic	triclinic	trigonal	monoclinic
Space group	P $2_1/n$	P -1	P -3	P $2_1/c$
a (Å)	17.3630(15)	10.0319(10)	21.4206(6)	10.7011(9)
b (Å)	16.1063(13)	11.2564(10)	21.4206(6)	14.0386(12)
c (Å)	23.308(2)	13.2929(12)	12.4219(7)	21.9492(18)
α (°)	90	85.795(2)	90	90
β (°)	109.489(3)	84.823(2)	90	94.437(2)
γ (°)	90	74.179(2)	120	90
V (Å^3)	6144.7(10)	1436.5(2)	4936.1(4)	3287.5(5)
Z	8	2	1	4
ρ_{calc} (g/cm$^{3)}$	1.557	1.729	1.637	1.729
μ (mm^{-1})	4.459	4.702	4.112	4.131
F(000)	2848	736	2406	1696
θ range (°)	1.57 to 25.73	1.54 to 27.16	1.10 to 27.17	1.72 to 26.45
Index ranges	-21 ⩽ h ⩽ 20 -16 ⩽ k ⩽ 19 -25 ⩽ l ⩽ 28	-12 ⩽ h ⩽ 12 -14 ⩽ k ⩽ 14 -17 ⩽ l ⩽ 17	-27 ⩽ h ⩽ 27 -20 ⩽ k ⩽ 25 -15 ⩽ l ⩽ 15	-12 ⩽ h ⩽ 13 -17 ⩽ k ⩽ 17 -27 ⩽ l ⩽ 27
Reflns coll.	51947	45400	44719	62970
Ind. reflns	11706 [R_{int} = 0.1262]	6371 [R_{int} = 0.0612]	7305 [R_{int} = 0.0465]	6774 [R_{int} = 0.0647]
Data / restraints / parameters	11706 / 30 / 717	6371 / 0 / 407	7305 / 0 / 424	6774 / 0 / 494
Goodness-of-fit on F^2	0.951	1.119	1.052	1.167
R_1 [I>2σ(I)]	0.0482	0.0281	0.0287	0.0380
wR_2 [all	0.0996	0.0711	0.0658	0.0888

data]				

Table S4. Crystal data for **4h**, **6h**, **7h**, **4i** and **4j**.

	4h	**6h**	**7h**	**4i**	**4j**
Chemical formula	$C_{30}H_{28}ClIrN_2O$	$C_{34}H_{30}ClIrN_2$	$C_{26}H_{18}ClF_2IrN_2$	$C_{28}H_{23}IrN_2O_2$	$C_{28}H_{20}F_3IrN_2O_2$
FW (g/mol)	660.19	694.25	624.07	611.68	665.66
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size (mm)	0.104 x 0.206 x 0.321	0.040 x 0.110 x 0.239	0.045 x 0.092 x 0.120	0.104 x 0.126 x 0.241	0.094 x 0.117 x 0.718
Crystal habit	red plate	red plate	red plate	red rod	orange rod
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	I 2/a	P 2_1/c	P 2_1/c	P -1	P 2_1/n
a (Å)	18.5540(7)	15.201(4)	11.5278(14)	9.1951(9)	13.4486(13)
b (Å)	9.8686(3)	10.767(2)	18.405(2)	15.8047(16)	9.1911(8)
c (Å)	26.8118(13)	16.947(4)	20.098(2)	16.8243(16)	19.9130(17)
α (°)	90	90	90	75.565(3)	90
β (°)	93.5610(10)	106.008(8)	102.572(3)	77.688(3)	104.962(3)
γ (°)	90	90	90	74.379(3)	90
V (Å^3)	4899.8(3)	2666.1(11)	4161.9(9)	2252.2(4)	2377.9(4)
Z	8	4	8	4	4
ρ_{calc} (g/cm^3)	1.790	1.730	1.992	1.804	1.859
μ (mm^{-1})	5.586	5.135	6.579	5.957	5.668
F(000)	2592	1368	2400	1192	1288
θ range (°)	2.20 to 28.28	2.27 to 27.93	1.52 to 25.74	1.26 to 28.37	2.11 to 29.61
Index ranges	-24 ⩽ h ⩽ 24 -13 ⩽ k ⩽ 11 -35 ⩽ l ⩽ 35	-20 ⩽ h ⩽ 19 -14 ⩽ k ⩽ 14 -19 ⩽ l ⩽ 22	-13 ⩽ h ⩽ 14 -19 ⩽ k ⩽ 22 -24 ⩽ l ⩽ 24	-12 ⩽ h ⩽ 12 -20 ⩽ k ⩽ 21 -22 ⩽ l ⩽ 22	-18 ⩽ h ⩽ 18 -12 ⩽ k ⩽ 12 -27 ⩽ l ⩽ 25
Reflns coll.	29298	31059	38290	45129	33902
Ind. reflns	6089 [R_{int} = 0.0419]	6377 [R_{int} = 0.0746]	7923 [R_{int} = 0.1077]	11221 [R_{int} = 0.0565]	6684 [R R_{int} = 0.0506]
Data / restraints / parameters	6089 / 0 / 316	6377 / 0 / 345	7923 / 0 / 535	11221 / 0 / 629	6684 / 0 / 323
Goodness-of-fit on F^2	1.040	1.015	1.032	1.005	1.026
R_1 [I>2σ(I)]	0.0239	0.0345	0.0516	0.0308	0.0284
wR_2 [all	0.0537	0.0711	0.1144	0.0629	0.0640

data]					

6. Computational Results

Optimized Structures

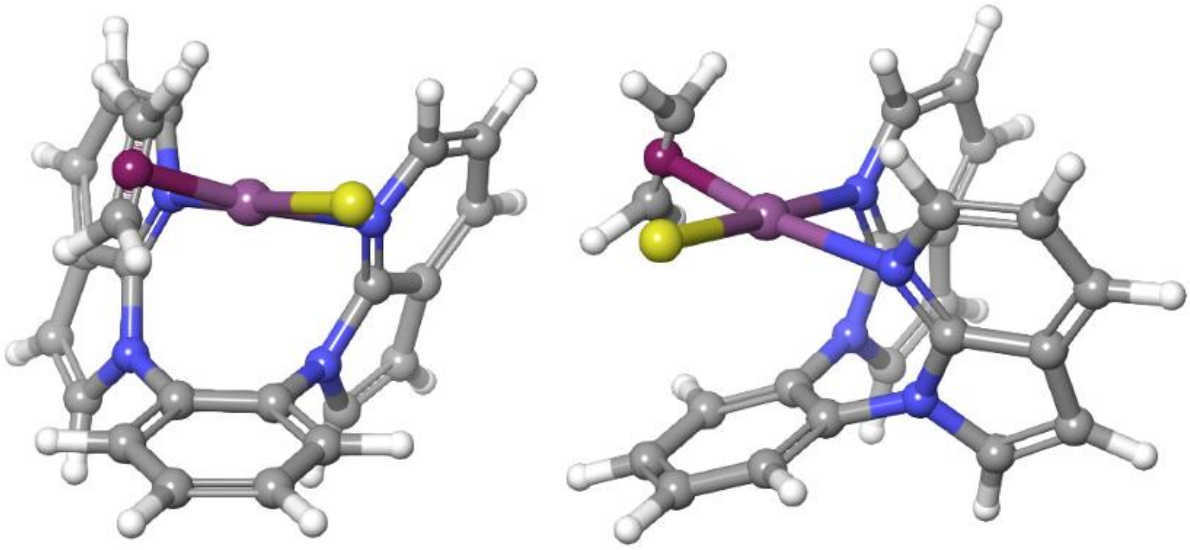

Figure S72. End-on and side-on angles of DFT-optimized (5-FP)Rh(C_2H_4)Cl (**1a**).

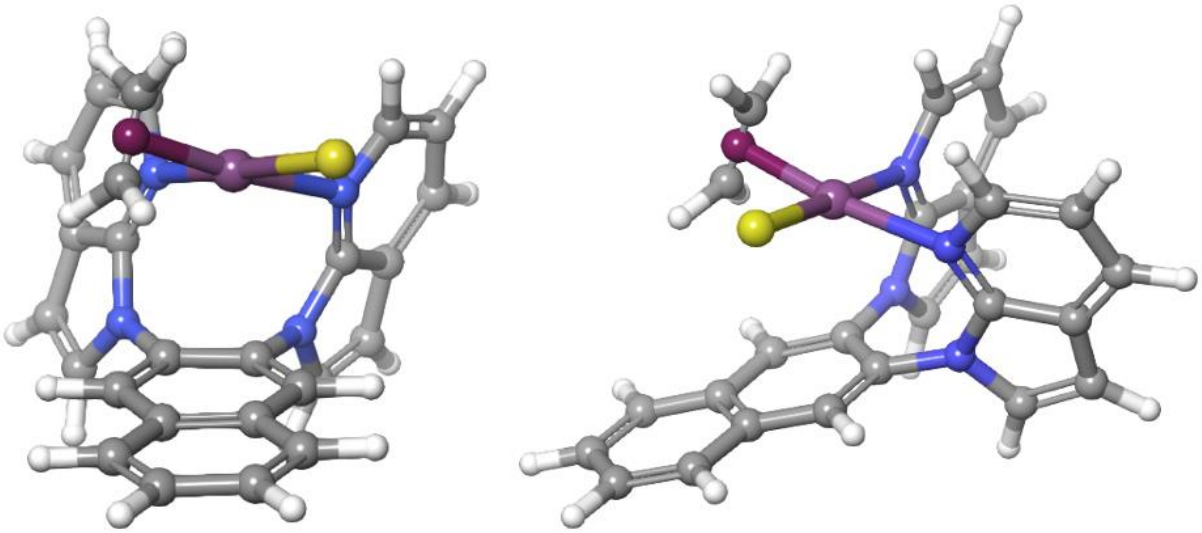

Figure S73. End-on and side-on angles of DFT-optimized (5-^{NP}FP)Rh(C_2H_4)Cl (**2a**).

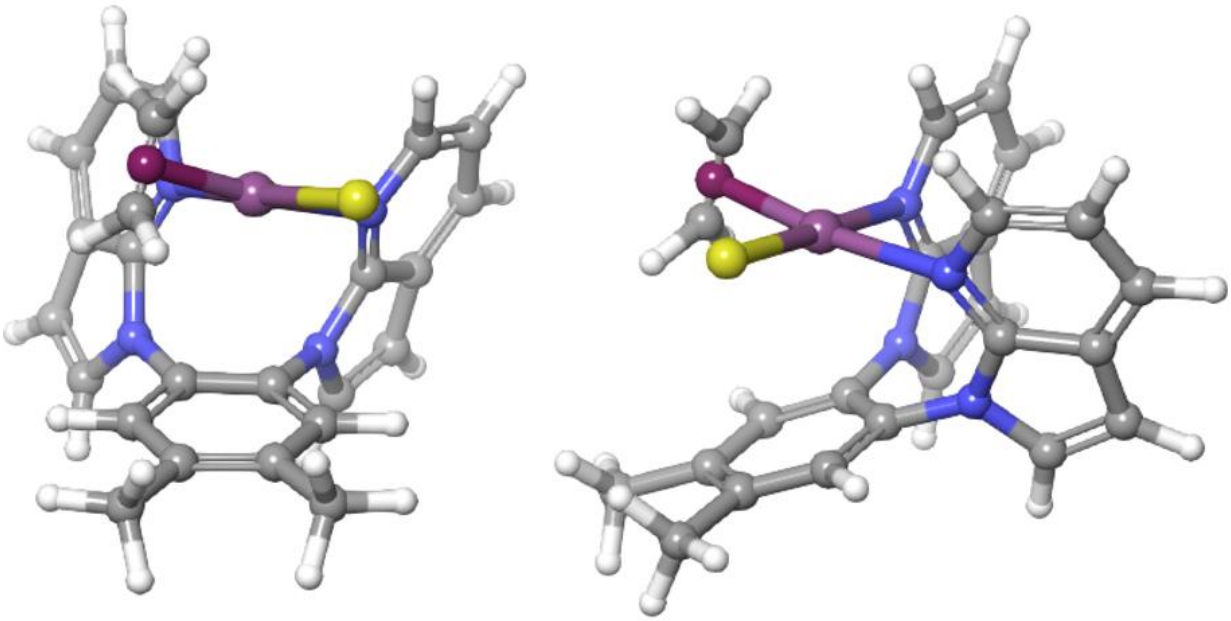

Figure S74. End-on and side-on angles of DFT-optimized (5-^{Me}FP)Rh(C_2H_4)Cl (**3a**).

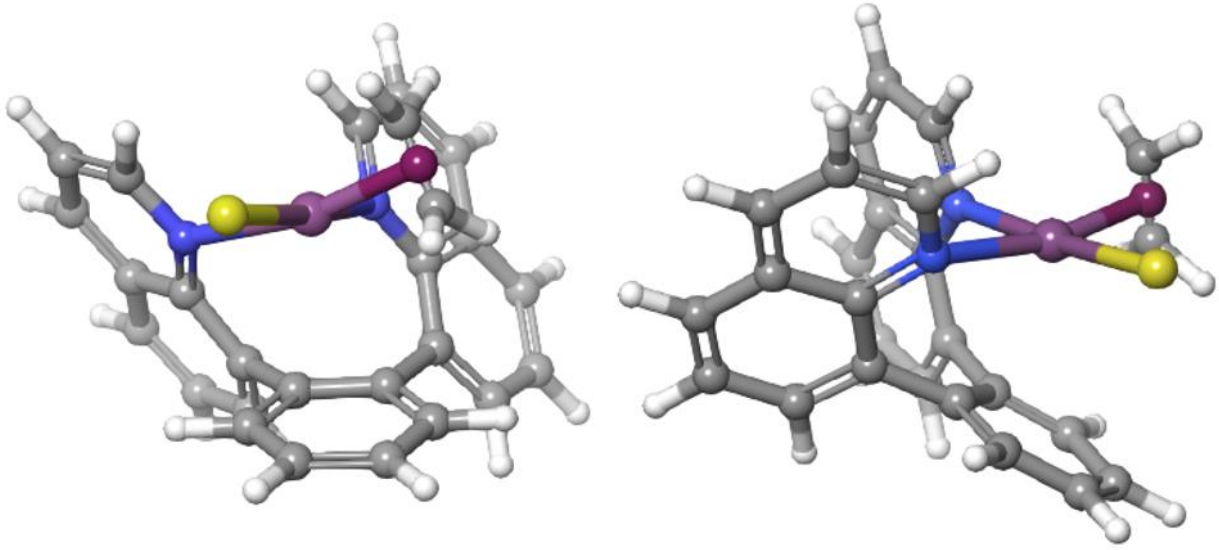

Figure S75. End-on and side-on angles of DFT-optimized (6-FP)Rh(C_2H_4)Cl (**4a**).

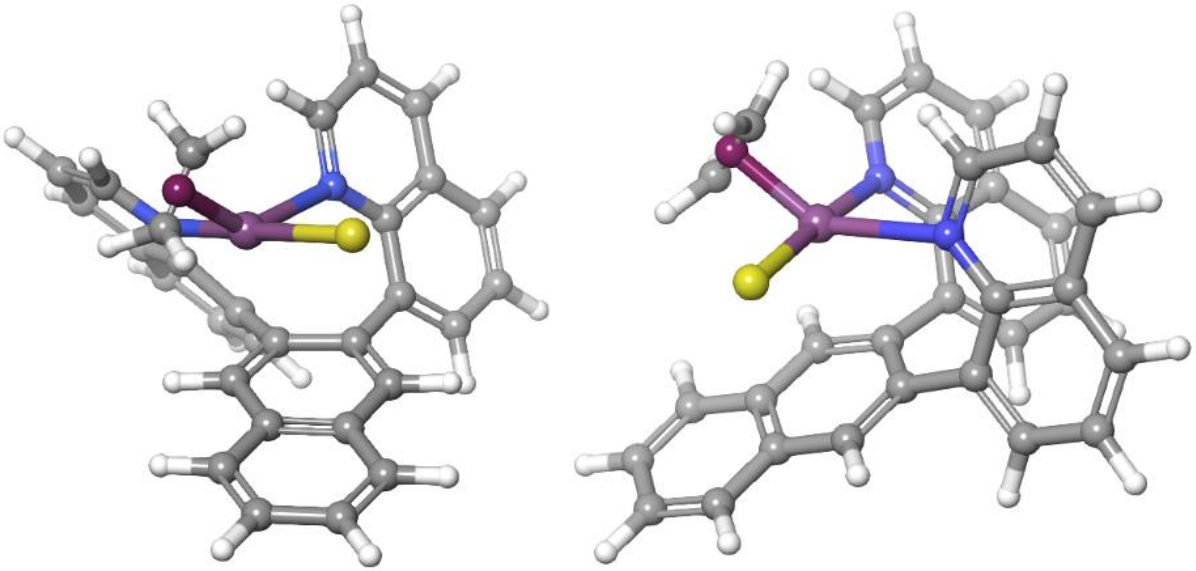

Figure S76. End-on and side-on angles of DFT-optimized (6-^{NP}FP)Rh(C_2H_4)Cl (**5a**).

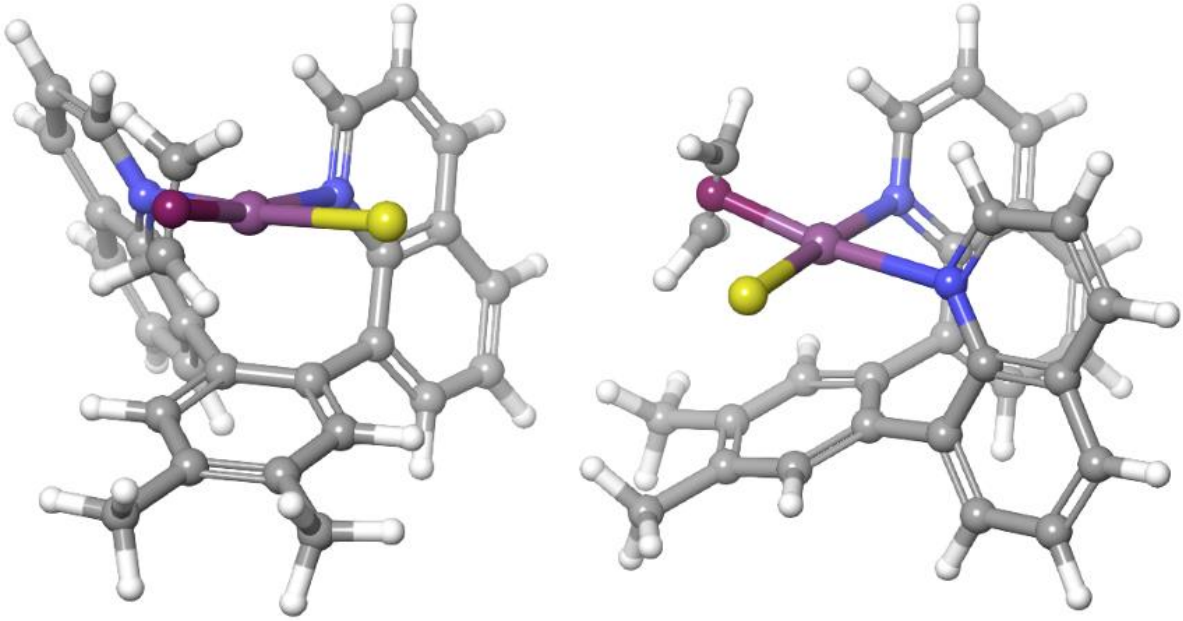

Figure S77. End-on and side-on angles of DFT-optimized (6-^{Me}FP)Rh(C_2H_4)Cl (**6a**).

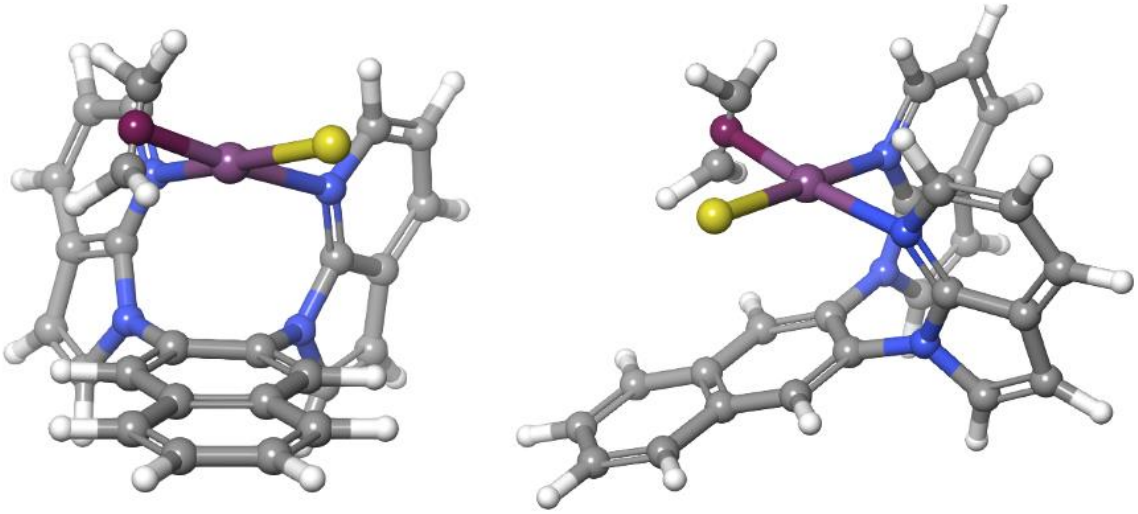

Figure S78. End-on and side-on angles of DFT-optimized (5-^{NP}FP)Ir(C_2H_4)Cl (**2h**).

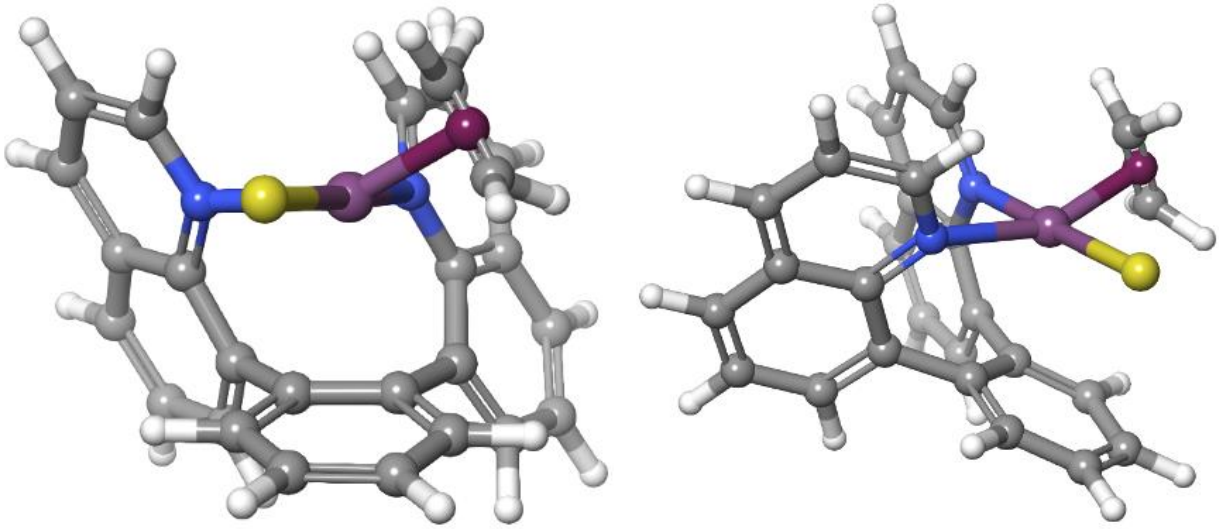

Figure S79. End-on and side-on angles of DFT-optimized (6-FP)Ir(C_2H_4)Cl (**4h**).

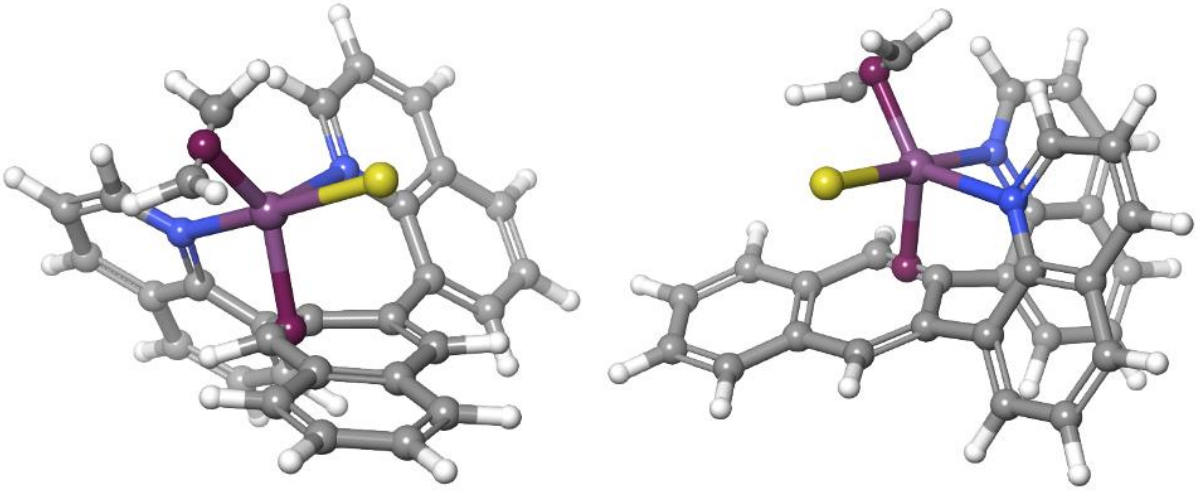

Figure S80. End-on and side-on angles of DFT-optimized (6-^{NP}FP)Ir(C_2H_4)Cl (**5h**).

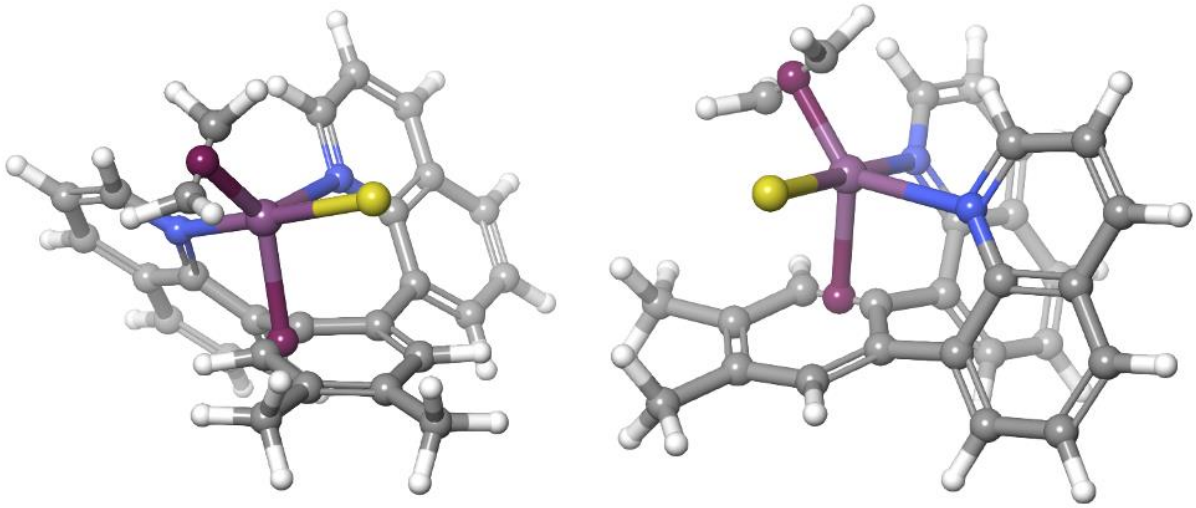

Figure S81. End-on and side-on angles of DFT-optimized (6-^{Me}FP)Ir(C_2H_4)Cl (**6h**).

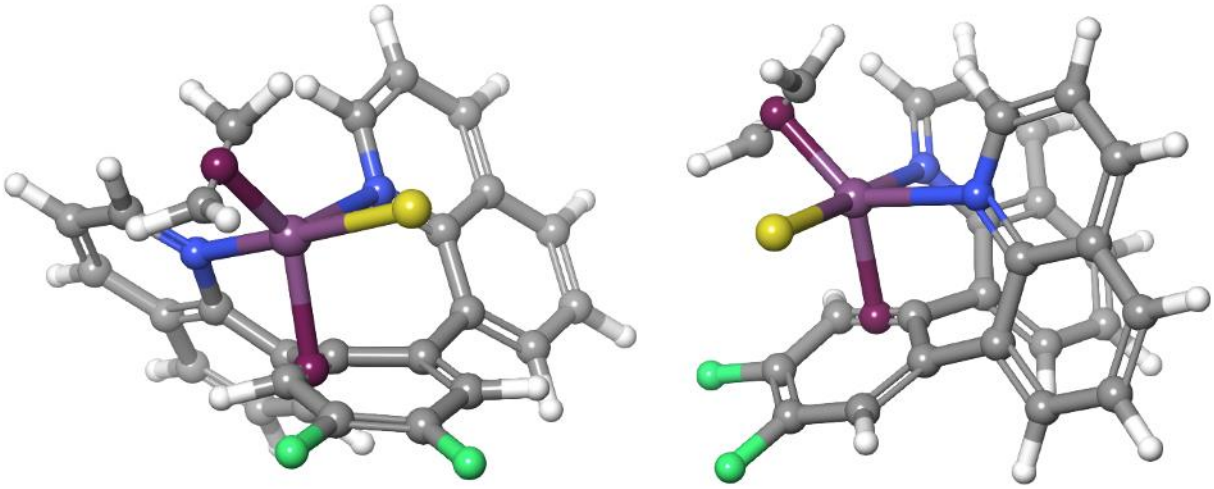

Figure S82. End-on and side-on angles of DFT-optimized (6-^{F}FP)Ir(C_2H_4)Cl (**7h**).

Optimized Structure coordinates:

(5-FP)Rh(C_2H_4)Cl (**1a**)

Rh1	24.3580092705	10.4704174280	5.6814862669
N2	23.2322031579	10.4560910029	7.5238871109
N3	22.2641813770	8.2250598647	7.4698337679
N4	21.1704428494	9.3438556918	5.1207630041
N5	22.4990929062	11.3209967042	4.7690034027
C6	23.2737507797	11.5775647869	8.2585141616
H7	23.8778680573	12.3812167882	7.8532425371
C8	22.6051258928	11.7402008889	9.4749215777
H9	22.7012500600	12.6842058015	9.9984189661
C10	21.8455098677	10.7015696230	9.9941520473
H11	21.3272208462	10.8037407882	10.9429760441
C12	21.7720911123	9.5216939267	9.2532095491
C13	22.4777628825	9.4670025401	8.0229359101
C14	21.1249565811	8.2510862013	9.4208372198
H15	20.5028587947	7.9395134652	10.2471961115
C16	21.4431917780	7.5031530708	8.3276403266
H17	21.1530422301	6.4963598088	8.0585898365
C18	22.7057660723	7.7665634313	6.1954302286
C19	22.1907369027	8.3473879402	5.0327036597
C20	22.6661854917	7.9491647914	3.7882233314
H21	22.2800819680	8.4299474177	2.8957001108
C22	23.6293015709	6.9476379181	3.7049697290
C23	24.1028427843	6.3338758052	4.8616822966
C24	23.6437829115	6.7439162161	6.1098771715
H25	24.0281231910	6.2985782689	7.0221293646
C26	19.8072282137	9.0859074351	5.2059643078
H27	19.4679492019	8.0719790262	5.3682092314
C28	19.0954595114	10.2383250626	5.0432126456
H29	18.0193036380	10.3286395871	5.0719257360
C30	20.0521250212	11.2891890434	4.8250690544
C31	21.3315811833	10.6890240982	4.8859337606
C32	20.0092811959	12.6642546581	4.5762309394
H33	19.0650299726	13.1977572531	4.5158821970
C34	21.2168919780	13.3280222161	4.4001301309
H35	21.2446667068	14.3910225805	4.1910292210
C36	22.4271959548	12.6302825328	4.5077528637

H37	23.3765897252	13.1418339887	4.3908304811
C38	26.1742432247	10.5900725558	6.7497065946
H39	26.8958485861	11.0936943973	6.1155311788
H40	26.0069851689	11.0442055748	7.7223597486
C41	25.8590839569	9.2500338990	6.5332747574
H42	25.4336656294	8.6527947063	7.3341077240
H43	26.3269013056	8.6892594431	5.7306899003
Cl44	25.5860111249	10.6470123291	3.5467961090
H46	24.0060498793	6.6448787578	2.7342339289
H47	24.8467639535	5.5465815654	4.7961353238

(5-^{NP}FP)Rh(C_2H_4)Cl (**2a**)

Rh1	24.3503372482	10.4545371522	5.6548888177
N2	23.2715267829	10.4388624306	7.5345799824
N3	22.2006043423	8.2550095364	7.4865756668
N4	21.1549286804	9.3401897856	5.1048146086
N5	22.4774919295	11.3254666868	4.7953815656
C6	23.3679261110	11.5555050394	8.2713861151
H7	24.0061042179	12.3315429952	7.8644186834
C8	22.7107530100	11.7493040073	9.4895992517
H9	22.8529247294	12.6873599379	10.0134160711
C10	21.9011609874	10.7490696007	10.0088055878
H11	21.3892025804	10.8761800810	10.9582071127
C12	21.7711163925	9.5740950331	9.2679242705
C13	22.4737129915	9.4855055186	8.0371495613
C14	21.0664610681	8.3346775461	9.4383429489
H15	20.4313709661	8.0535622838	10.2662247464
C16	21.3499241264	7.5710333613	8.3458591974
H17	21.0176373765	6.5761905166	8.0794837116
C18	22.6690787660	7.7636454154	6.2358528909
C19	22.1809413862	8.3496294631	5.0336966561
C20	22.6885322242	7.9629941815	3.8237365257
H21	22.3335464821	8.4375952435	2.9127291495
C22	23.6799165622	6.9503268628	3.7526892535
C23	24.1122653360	6.3158420521	4.9496745658
C24	23.5875857545	6.7526347251	6.1938293896
H25	23.9504166748	6.3147303804	7.1200826314
C26	19.7923271355	9.0762594391	5.1779656923
H27	19.4552970559	8.0584677798	5.3219602797
C28	19.0774668462	10.2286083783	5.0276570352
H29	18.0009620847	10.3154448733	5.0457557770
C30	20.0318867136	11.2862398421	4.8357760471
C31	21.3123314341	10.6892728028	4.8958089854

C32	19.9858149489	12.6646080276	4.6110153378
H33	19.0400727188	13.1952705387	4.5522671782
C34	21.1923896855	13.3353607263	4.4571167185
H35	21.2184434114	14.4020228953	4.2681008761
C36	22.4035384146	12.6388513235	4.5600141568
H37	23.3517633261	13.1547446291	4.4583832315
C38	26.1986983443	10.5424823175	6.6693517372
H39	26.9011636753	11.0617144913	6.0258855940
H40	26.0632772750	10.9703541610	7.6593175689
C41	25.8728232201	9.2084431591	6.4258859177
H42	25.4707457074	8.5918117576	7.2240925903
H43	26.3144030248	8.6688074040	5.5935259148
Cl44	25.5102129635	10.6565296330	3.4840140828
C45	25.0892378293	5.2890070882	4.8762753227
H46	25.4167077727	4.8088143403	5.7941060440
C47	25.6128742061	4.9177690440	3.6635964738
H48	26.3616725038	4.1344149742	3.6114757156
C49	25.1868685130	5.5546390502	2.4706788753
H50	25.6173053807	5.2531106828	1.5205322636
C51	24.2416101047	6.5464979355	2.5128200879
H52	23.9151711627	7.0396774395	1.6016853550

(5-^{Me}FP)Rh(C_2H_4)Cl (**3a**)

Rh1	24.3386839863	10.4324949148	5.6601351438
N2	23.2380195282	10.4333442466	7.5241818225
N3	22.2257375944	8.2209808404	7.4956850568
N4	21.1422716720	9.3059859199	5.1141209861
N5	22.4704375984	11.2829753190	4.7664617253
C6	23.3125257989	11.5557632280	8.2546226442
H7	23.9249602043	12.3463729315	7.8363521983
C8	22.6680446987	11.7351106162	9.4820726267
H9	22.7910264566	12.6782284274	10.0014643964
C10	21.8976462157	10.7130768954	10.0175236965
H11	21.4004682848	10.8276575667	10.9763442711
C12	21.7872002303	9.5328392169	9.2811487388
C13	22.4714584215	9.4608478069	8.0388385477
C14	21.1198541135	8.2752499412	9.4646197906
H15	20.5061937572	7.9782160573	10.3025100792
C16	21.4076200461	7.5173678028	8.3689970210
H17	21.0986468923	6.5133758193	8.1103501988
C18	22.6672634363	7.7470733874	6.2280966754
C19	22.1693148170	8.3149212149	5.0579429868
C20	22.6817439029	7.9131839123	3.8291439633

H21	22.3067101426	8.3890117225	2.9275610144
C22	23.6671551125	6.9321498394	3.7485827946
C23	24.1237008538	6.3156209270	4.9287585584
C24	23.6177639820	6.7353582861	6.1562803576
H25	23.9886139365	6.3010604174	7.0808960143
C26	19.7800964138	9.0476646446	5.1987918369
H27	19.4414520645	8.0329038921	5.3581416972
C28	19.0666880176	10.1994458331	5.0335552534
H29	17.9902743124	10.2882921558	5.0586074934
C30	20.0227856303	11.2505446874	4.8164312105
C31	21.3027988996	10.6508512267	4.8811078282
C32	19.9807564708	12.6256896134	4.5689363411
H33	19.0366361311	13.1589920585	4.5064765141
C34	21.1884451305	13.2896219373	4.3965816633
H35	21.2161854223	14.3527381884	4.1892708625
C36	22.3985869920	12.5919714287	4.5063431977
H37	23.3482808023	13.1033826103	4.3924890099
C38	26.1748626017	10.5510451742	6.7025315638
H39	26.8819800673	11.0592518085	6.0546925909
H40	26.0198465615	11.0034114254	7.6789803767
C41	25.8567588643	9.2106276291	6.4873887348
H42	25.4405765847	8.6115521220	7.2925805880
H43	26.3074982659	8.6532233516	5.6716813653
Cl44	25.5362255827	10.5820867915	3.5001175504
C46	24.2430076404	6.5465276631	2.4134174215
C47	25.1755707458	5.2400258316	4.8724525068
H48	24.1551153961	5.4696548079	2.2379751870
H49	23.7381914084	7.0735738812	1.6019744139
H50	25.3080386530	6.7978749892	2.3701866891
H51	25.4394995161	4.8969250471	5.8737291075
H52	24.8288026030	4.3770286982	4.2957520461
H53	26.0830500022	5.6074183324	4.3847100061

(6-FP)Rh(C_2H_4)Cl (**4a**)

Rh1	10.3411344963	3.2975058616	18.0406010752
Cl2	8.1372372070	2.2085889647	18.2505897553
N3	12.2346971283	4.3827747135	18.0116917238
N4	9.3674859069	5.3169273594	17.6310307145
C5	11.1251947405	1.9579313507	19.4609965496
H6	11.9311153841	2.4228591483	20.0230024810
H7	10.3017900520	1.5765399880	20.0558667631
C8	11.3555335301	1.4608078850	18.1738711575
H9	10.7169502711	0.6915182983	17.7516004560

H10	12.3384917384	1.5518561882	17.7198471719
C11	12.4647002798	4.9860772243	19.1649709237
H12	11.6662801922	4.9303576853	19.8977356238
C13	13.6641052601	5.6496026310	19.4896155094
H14	13.7656581373	6.1177429030	20.4614083268
C15	14.6745391319	5.6471525038	18.5695691771
H16	15.6334550290	6.1118585622	18.7819261654
C17	14.4701450729	5.0271584444	17.3128754521
C18	13.2083531692	4.4243646825	17.0383765453
C19	15.5028192993	5.0035168690	16.3397653527
H20	16.4549115941	5.4671544046	16.5801086277
C21	15.2911574573	4.4049666790	15.1285871197
H22	16.0755632164	4.3744255298	14.3801074564
C23	14.0263960409	3.8483627267	14.8354872669
H24	13.8526848595	3.4227381730	13.8521085047
C25	12.9857911860	3.8620398659	15.7393867775
C26	11.6663179496	3.3248351960	15.3073017328
C27	11.5712361501	1.9955509747	14.8844567431
H28	12.4598957958	1.3720609606	14.9041936555
C29	10.3538778418	1.4613886624	14.4784792307
H30	10.2953286999	0.4241682641	14.1659624093
C31	9.2116223256	2.2568651164	14.4909033650
H32	8.2535088740	1.8452348928	14.1934872195
C33	9.3010102562	3.5881110686	14.8814050942
H34	8.4158938294	4.2161709142	14.8769049127
C35	10.5228017319	4.1416224157	15.2768192280
C36	10.5832994012	5.6067433302	15.5688115483
C37	11.2147888052	6.4612145885	14.6935738335
H38	11.7293230261	6.0468278218	13.8321622317
C39	11.1774044022	7.8649042431	14.8691937498
H40	11.6894395738	8.5028535866	14.1566803107
C41	10.4689622796	8.4123182041	15.9063864753
H42	10.4012955443	9.4887401315	16.0321280873
C43	9.8090042177	7.5695774037	16.8376297487
C44	9.9047135318	6.1609797823	16.6959302869
C45	9.0458839695	8.0787860948	17.9206829215
H46	8.9435359129	9.1542220012	18.0393096198
C47	8.4442098009	7.2102375375	18.7899746084
H48	7.8390341422	7.5558684957	19.6195973652
C49	8.6552732684	5.8223400422	18.6148051886
H50	8.2379381304	5.1068418014	19.3171922202

(6-^{NP}FP)Rh(C_2H_4)Cl (**5a**)

Rh1	25.5022425654	9.2203302297	5.4410238377
Cl2	26.3264430777	9.4609313626	3.1313933574
N3	23.8583211859	11.0374635135	5.0806393341
N4	24.6669209633	9.0750586664	7.4082949343
C5	24.3204937801	12.1212379633	5.6655674874
H6	25.2429623379	12.0046601839	6.2276733300
C7	23.7015805108	13.3898932767	5.5915298598
H8	24.1503808578	14.2343574380	6.1013367160
C9	22.5512446931	13.5100538074	4.8625210551
H10	22.0401880526	14.4642100410	4.7651424388
C11	22.0156634562	12.3683715899	4.2154705598
C12	20.8323813343	12.4437646024	3.4350229862
H13	20.3259628304	13.4004807004	3.3442702116
C14	20.3514284638	11.3258114168	2.8085203198
H15	19.4495502098	11.3749715643	2.2077037288
C16	21.0261358880	10.0907256432	2.9488897382
H17	20.6235627254	9.2084419904	2.4607155538
C18	22.1701096419	9.9683099833	3.7053157343
C19	22.7015389937	11.1298904990	4.3553992202
C20	22.8604812491	8.6590243864	3.8105223827
C21	23.1783850008	8.0991626170	5.0954264211
C22	23.9537515179	6.9562493885	5.1583445843
H23	24.1721918146	6.5092613139	6.1247737489
C24	24.3764946852	6.2747017592	3.9832214135
C25	25.1436619271	5.0841002007	4.0449922948
H26	25.4317503916	4.6920051351	5.0164446866
C27	25.5151581028	4.4376829195	2.8918606981
H28	26.1015141483	3.5260755864	2.9421083146
C29	25.1373229853	4.9563870492	1.6296310692
H30	25.4404889639	4.4370264652	0.7263473044
C31	24.3966621864	6.1094646607	1.5455596972
H32	24.1130120504	6.5148007885	0.5788344171
C33	23.9950325701	6.7934503485	2.7207480986
C34	23.2517691243	8.0038795422	2.6710979473
H35	23.0384190104	8.4436590600	1.7008420861
C36	22.5339665779	8.6014669996	6.3459587962
C37	21.1590085828	8.6043366318	6.4358498165
H38	20.5764588130	8.3175676879	5.5658883045
C39	20.4888327882	8.9268516281	7.6375430487
H40	19.4041959538	8.9208120533	7.6611662940
C41	21.2081254020	9.2009705006	8.7699590465
H42	20.7135477592	9.4110928455	9.7135339767
C43	22.6260076142	9.2106877537	8.7261262048

C44	23.4062022620	9.4521001047	9.8847021033
H45	22.9094461301	9.6243381653	10.8356653918
C46	24.7693497074	9.4480890426	9.7854329352
H47	25.4111881975	9.6044949361	10.6440996289
C48	25.3559375937	9.2760620477	8.5136556695
H49	26.4347077124	9.3242307704	8.4233168759
C50	23.2954011040	8.9650114375	7.4975284829
C51	27.2404406005	8.2538945634	6.0060229461
H52	27.1027648211	7.6829779346	6.9216483195
C53	27.4318062887	9.6590934830	6.0591694743
H54	27.4712241488	10.1933320398	7.0041411459
H55	27.6491211009	7.6859491753	5.1754918430
H56	27.9681008188	10.1489699081	5.2539721061

(6-^{Me}FP)Rh(C_2H_4)Cl (**6a**)

Rh1	0.9372020416	4.8877211401	9.3785247412
Cl2	2.2291288344	6.9357086506	9.9370310221
N3	2.7918255184	4.0355748607	8.3552928408
N4	-0.0012674861	3.0566981291	8.6756659453
C5	-0.6524906796	5.4831732538	10.6247692371
H6	-1.2577829240	4.6234519609	10.8963930215
H7	-0.2036189699	6.0219210371	11.4546240953
C8	-0.8086611648	6.0903264172	9.3776208808
H9	-0.4834499588	7.1137827953	9.2246861862
H10	-1.5709357483	5.7408612714	8.6870208207
C11	2.7636171487	4.2448362955	7.0544908005
H12	1.8431917178	4.6608687116	6.6553711893
C13	3.8459399644	3.9807559004	6.1880541234
H14	3.7432827812	4.1816482533	5.1281162589
C15	5.0038304329	3.4946401078	6.7286595567
H16	5.8744131044	3.2922224452	6.1104657416
C17	5.0757950857	3.2515519941	8.1227121762
C18	6.2641675080	2.7624008246	8.7241041793
H19	7.1275205964	2.5703191720	8.0937611430
C20	6.3089506212	2.5477241962	10.0745540604
H21	7.2136787950	2.1807090206	10.5470694073
C22	5.1608573488	2.7870742108	10.8637570356
H23	5.1999632435	2.5827258709	11.9290925855
C24	3.9788167767	3.2466368184	10.3247077400
C25	3.9268966071	3.5171468296	8.9202137488
C26	2.8119484644	3.4244322273	11.2331341897
C27	1.6353085265	2.6786509748	11.0894615938
C28	0.6222320197	2.8148771882	12.0450552935

H29	-0.2783632655	2.2145039000	11.9367152013
C30	0.7319074416	3.6917920328	13.1179474214
C31	1.9000064953	4.4651238774	13.2461050928
C32	2.9178773952	4.3089643030	12.3121530802
H33	3.8179307839	4.9103237266	12.4025431407
C34	2.0399090265	5.4569209183	14.3709674154
H35	1.2519266440	6.2144192533	14.3232352037
H36	3.0023533536	5.9682774228	14.3246592474
H37	1.9565694951	4.9681221425	15.3462475523
C38	-0.3910878572	3.8276166146	14.1124133968
H39	-1.2152670492	3.1553368824	13.8679989309
H40	-0.7778402674	4.8513889505	14.1243403892
H41	-0.0550445470	3.6011265917	15.1291905536
C42	1.4580414557	1.6433274082	10.0275627011
C43	2.0937718383	0.4307044321	10.1768366701
H44	2.7687068877	0.2982011850	11.0170318123
C45	1.8649121343	-0.6513998438	9.2975599313
H46	2.3880437676	-1.5884699311	9.4552867572
C47	0.9589972020	-0.5195326849	8.2802123402
H48	0.7367509072	-1.3470074242	7.6130573626
C49	0.2905339636	0.7148639939	8.0777441013
C50	-0.6546808624	0.8732280724	7.0334570867
H51	-0.8831382085	0.0272777370	6.3909626864
C52	-1.2566534079	2.0860687304	6.8550248708
H53	-1.9890597917	2.2598419372	6.0755462172
C54	-0.8730392919	3.1569660340	7.6904524783
H55	-1.2863184867	4.1408415721	7.5084034576
C56	0.5660623615	1.8237271969	8.9260459261

(5-^{NP}FP)Ir(C_2H_4)Cl (**2h**)

Ir1	24.3159200889	10.5043261924	5.7366056113
N2	23.3282374267	10.4980353682	7.5636252519
N3	22.2725151128	8.2977638763	7.4469900529
N4	21.1559060772	9.3177295416	5.0384887903
N5	22.4715348496	11.3377049387	4.8924931515
C6	23.4333762621	11.5841827030	8.3504646348
H7	24.0569611500	12.3782026864	7.9593993324
C8	22.7996617418	11.7162253564	9.5873069989
H9	22.9463285999	12.6318307955	10.1481638132
C10	22.0062152804	10.6891351974	10.0758982784
H11	21.5094023966	10.7691281855	11.0380757428
C12	21.8710494770	9.5468200907	9.2862505915
C13	22.5486964987	9.5088497247	8.0392638755

C14	21.1756535294	8.2988071806	9.4230642658
H15	20.5566300293	7.9859510541	10.2513287796
C16	21.4439664331	7.5778726072	8.2996079011
H17	21.1145225174	6.5905483968	8.0048672462
C18	22.7320469774	7.8039956375	6.1906487163
C19	22.1916920001	8.3324829040	4.9843779806
C20	22.6417329857	7.8868204372	3.7725694098
H21	22.2364918341	8.3124283048	2.8585808921
C22	23.6363288786	6.8772504492	3.7026341105
C23	24.1350114727	6.3118223463	4.9079045827
C24	23.6582509796	6.7995763089	6.1520059432
H25	24.0574900557	6.3986321684	7.0797670547
C26	19.7973466845	9.0353271919	4.9551662194
H27	19.4656027583	8.0098272631	5.0382958116
C28	19.0840689233	10.1800520803	4.7580242113
H29	18.0107411064	10.2533669261	4.6657631901
C30	20.0357377445	11.2542534232	4.6898969722
C31	21.3129802873	10.6732181024	4.8726630091
C32	19.9848846401	12.6338483743	4.4788659712
H33	19.0394891543	13.1475263898	4.3330854142
C34	21.1868407348	13.3275973161	4.4485180124
H35	21.2113281436	14.3961164730	4.2724637140
C36	22.3950158035	12.6545229085	4.6565486592
H37	23.3393127600	13.1853789607	4.6456666023
C38	26.1478135262	10.6214781769	6.6988248858
H39	26.8897713783	11.0944709086	6.0606111361
H40	26.0826590980	11.0439381955	7.7005539597
C41	25.8043907004	9.2598958450	6.4849882903
H42	25.4641668854	8.6577421992	7.3250393661
H43	26.2798101551	8.6903588577	5.6905165676
Cl44	25.4069178450	10.6361331953	3.5558308481
C45	25.1155084991	5.2879739764	4.8383254081
H46	25.4969434978	4.8617855954	5.7616686142
C47	25.5750159800	4.8509198865	3.6221605017
H48	26.3242510175	4.0679273954	3.5741416526
C49	25.0788434380	5.4161082398	2.4208669631
H50	25.4549982445	5.0596318338	1.4679828966
C51	24.1317535603	6.4066539900	2.4589933042
H52	23.7509050005	6.8460165212	1.5421113856

(6-FP)Ir(C_2H_4)Cl (**4h**)

Ir1	10.4369127719	3.3333782523	17.9624541341
Cl2	8.2804397854	2.1874042893	17.8287194162

N3	12.2139197790	4.3805383403	18.1361523952
N4	9.4662993705	5.3586100087	17.7181028835
C5	10.9187627417	2.1990150958	19.5979215393
H6	11.6278856652	2.6584710196	20.2861590433
H7	10.0443928091	1.7848549311	20.0934027175
C8	11.4076666730	1.5693931448	18.3958783546
H9	10.8981506659	0.6913718423	18.0067341606
H10	12.4767391315	1.5822660687	18.1884853262
C11	12.4563121876	4.9843722662	19.2899236156
H12	11.6679000484	4.9215182424	20.0306837708
C13	13.6586222875	5.6523833240	19.5904731442
H14	13.7731211207	6.1166959170	20.5629636610
C15	14.6546636551	5.6616098259	18.6550265223
H16	15.6140072348	6.1310126678	18.8550753603
C17	14.4302113979	5.0498298792	17.3977088253
C18	13.1705369371	4.4407534993	17.1412714304
C19	15.4388053159	5.0379402150	16.4005997047
H20	16.3954900818	5.5014087732	16.6225259924
C21	15.1990227611	4.4502238243	15.1889796148
H22	15.9656257884	4.4285486463	14.4218766550
C23	13.9295436647	3.8930225561	14.9185095256
H24	13.7356256632	3.4766087810	13.9349762294
C25	12.9139563010	3.8911497763	15.8497787130
C26	11.5818989966	3.3639431273	15.4307874449
C27	11.4831104383	2.0317747340	14.9964296247
H28	12.3515852691	1.3868755218	15.0875114290
C29	10.2980194333	1.5376638295	14.4776069850
H30	10.2375371960	0.5011854128	14.1618318519
C31	9.1834254638	2.3709371138	14.3719911900
H32	8.2481514505	1.9868688290	13.9797410490
C33	9.2738023809	3.6955796748	14.7710027397
H34	8.4133165401	4.3516118789	14.6795027264
C35	10.4674514851	4.2158582422	15.2915867295
C36	10.5250399051	5.6849774091	15.5781018189
C37	11.0606854349	6.5539071110	14.6558032801
H38	11.5224361350	6.1534663175	13.7588424751
C39	10.9906013374	7.9570112772	14.8319351828
H40	11.4306338366	8.6086666394	14.0842894441
C41	10.3372078714	8.4839510060	15.9145003942
H42	10.2391910116	9.5578666121	16.0421153392
C43	9.7709506426	7.6236022515	16.8910204603
C44	9.9086716750	6.2200128368	16.7469557015
C45	9.0567939128	8.1106204895	18.0149450002

H46	8.9227987815	9.1819955454	18.1370330599
C47	8.5404849449	7.2222202213	18.9206213612
H48	7.9732336251	7.5469001725	19.7847130767
C49	8.7947357031	5.8437685510	18.7412380808
H50	8.4582774793	5.1206044160	19.4775011427

(6-^{NP}FP)Ir(C_2H_4)Cl (**5h**)

Ir1	25.3439117604	9.1462846095	5.4489668379
Cl2	26.1258886907	9.3436553152	3.1427675490
N3	23.9747701263	11.0857888111	5.0773403033
N4	24.6360287852	9.1083393275	7.4008331303
C5	24.4711019411	12.1679821602	5.6412366337
H6	25.3835656747	12.0339188408	6.2139996320
C7	23.9002162121	13.4537335270	5.5309844580
H8	24.3765605439	14.2925992065	6.0243038807
C9	22.7620102495	13.5947758082	4.7885231467
H10	22.2858186642	14.5631591484	4.6620030804
C11	22.1901649825	12.4578934243	4.1646687998
C12	21.0146885573	12.5745825864	3.3777400296
H13	20.5544746586	13.5524418973	3.2710377836
C14	20.4831760734	11.4701658242	2.7695507851
H15	19.5847143965	11.5487597518	2.1668443345
C16	21.1015777364	10.2112076503	2.9345902009
H17	20.6603365008	9.3388516698	2.4627390226
C18	22.2405520908	10.0452989130	3.6920971106
C19	22.8226811843	11.1933147746	4.3338707233
C20	22.8786980721	8.7140001446	3.8012879744
C21	23.3458404824	8.2817273168	5.1124124985
C22	24.2865729353	7.2134838050	5.1876879773
H23	24.4069604413	6.6958219153	6.1355906475
C24	24.5672966904	6.4222117918	3.9964506247
C25	25.3776239163	5.2773492440	4.0604566563
H26	25.8218054636	4.9971176940	5.0116995833
C27	25.6152090658	4.5173181243	2.9284893083
H28	26.2460436211	3.6365568108	2.9871853484
C29	25.0396573721	4.8860124981	1.7021699556
H30	25.2291241659	4.2905642299	0.8151147444
C31	24.2341022436	6.0070599543	1.6253375347
H32	23.7916426890	6.2992273846	0.6772940762
C33	23.9787051130	6.7893432467	2.7673820478
C34	23.1746868390	7.9868894174	2.6958530813
H35	22.8860698305	8.3517754058	1.7138239700
C36	22.5572612097	8.6070751320	6.3352496780

C37	21.1856216001	8.5242859470	6.4010259477
H38	20.6225719331	8.2684598790	5.5088204946
C39	20.5002069361	8.7341644672	7.6223268617
H40	19.4176660148	8.6648906203	7.6395536551
C41	21.1912390592	8.9885315271	8.7795840725
H42	20.6731920220	9.1217894035	9.7242940144
C43	22.6070750334	9.0866657604	8.7534940960
C44	23.3937984910	9.3323663582	9.9066204132
H45	22.9106837630	9.4412082364	10.8735371024
C46	24.7540038880	9.4187839572	9.7791794637
H47	25.3992277093	9.5890181374	10.6328164423
C48	25.3398604744	9.3151709398	8.4993409056
H49	26.4121219455	9.4200219988	8.3925136430
C50	23.2727683126	8.9368140197	7.5154622622
C51	27.1778955054	8.3781586977	5.9811380776
H52	27.1791554916	7.8490538969	6.9327434625
C53	27.2481746341	9.8250219370	5.9722298518
H54	27.3239232624	10.3726318992	6.9086212580
H55	27.6548889159	7.8248470558	5.1766621595
H56	27.7612720313	10.3077959408	5.1473427431

(6-^{Me}FP)Ir(C_2H_4)Cl (**6h**)

Ir1	0.7687937509	4.6576910976	9.6375100552
Cl2	1.8460258315	6.5774797895	10.7082290598
N3	2.8596099738	4.1504856457	8.4430184002
N4	-0.0420249691	3.0228171546	8.6623156009
C5	-1.0420002459	5.5881468094	9.8161681750
H6	-1.9064579999	4.9319162859	9.7196078738
H7	-1.1127762530	6.2635214205	10.6656500094
C8	-0.3573276999	6.0453572518	8.6166434761
H9	0.0826306897	7.0381143217	8.6297981423
H10	-0.7195654715	5.7602887410	7.6310134083
C11	2.7591577403	4.5266519991	7.1853157225
H12	1.8006709462	4.9405728958	6.8876292084
C13	3.8073870206	4.4338734393	6.2427970350
H14	3.6422181372	4.7688072718	5.2253533676
C15	5.0095597243	3.9326919388	6.6560678202
H16	5.8526623729	3.8512375388	5.9749613215
C17	5.1646672904	3.5143703750	8.0011152886
C18	6.3991550973	3.0000726467	8.4758415447
H19	7.2327001947	2.9205660448	7.7837597399
C20	6.5261002874	2.6179867086	9.7843208218
H21	7.4674291025	2.2269562977	10.1556420391

C22	5.4224244874	2.7216159339	10.6606385822
H23	5.5308330866	2.4006466552	11.6923155854
C24	4.2010244769	3.2007547724	10.2418925661
C25	4.0498437101	3.6268493202	8.8788893491
C26	3.0715580985	3.3341231479	11.1861123228
C27	1.7783618267	2.8614237248	10.8175281652
C28	0.6775405186	3.2403534246	11.6192077709
H29	-0.2860701045	2.7731917535	11.4396302582
C30	0.8564503882	3.9654103263	12.8240404465
C31	2.1334263114	4.3347814261	13.2078915166
C32	3.2244343625	4.0320145079	12.3637460569
H33	4.2048158498	4.4293214650	12.6132048798
C34	2.3553532969	5.1445053303	14.4580156195
H35	1.8763044853	6.1254270814	14.3683887550
H36	3.4183822526	5.3035705516	14.6388013165
H37	1.9281213722	4.6538706139	15.3374855432
C38	-0.3507126743	4.3621437318	13.6316255469
H39	-1.2591980901	3.9247325054	13.2187364108
H40	-0.4685192291	5.4518030595	13.6238076856
H41	-0.2647203564	4.0555108359	14.6783019639
C42	1.6050523177	1.7367338534	9.8536662715
C43	2.3214349957	0.5678573838	9.9803979628
H44	3.0794195693	0.4951562842	10.7539393863
C45	2.0621027132	-0.5479287263	9.1518492252
H46	2.6496505519	-1.4510477235	9.2781251300
C47	1.0518796802	-0.5038321407	8.2261864762
H48	0.8168605106	-1.3662432928	7.6098126950
C49	0.2894566305	0.6810206653	8.0615258021
C50	-0.7852312110	0.7774193730	7.1424832585
H51	-1.0529912648	-0.0848164224	6.5381459938
C52	-1.4727249715	1.9556102062	7.0472856552
H53	-2.3147008962	2.0760324082	6.3759710446
C54	-1.0577231341	3.0626687476	7.8159906011
H55	-1.5761847786	4.0062594691	7.7086827052
C56	0.6051801039	1.8157635452	8.8473652364

(6-^{F}FP)Ir(C_2H_4)Cl (**7h**)

Ir1	1.2715875736	12.1517417618	15.5280761666
Cl2	0.6516865737	10.0443141766	16.5931632030
F3	-2.6930511731	11.8704319064	14.8341931385
F4	-2.5236129296	9.2383725393	14.2602928318
N5	1.9243278056	13.8910516222	14.5988974008
N6	3.2024829394	11.0303546211	14.5717619598

C7	1.7730552757	12.7947144908	17.4352604335
H8	1.9115606731	11.9753956922	18.1333436317
H9	2.5569163373	13.5458006359	17.4977316340
C10	0.4185836701	13.1791601482	17.0906976188
H11	0.1973870041	14.2229681731	16.8747425573
H12	-0.4085173863	12.6513485458	17.5577604378
C13	2.3231699950	14.9976369650	15.2009731831
H14	2.2022458661	15.0534174315	16.2753144363
C15	2.9042016417	16.0833405190	14.5122646819
H16	3.2066142987	16.9550254616	15.0802905364
C17	3.0965095664	15.9972750308	13.1599890700
H18	3.5707191277	16.8018896605	12.6051582672
C19	2.6545153529	14.8386256622	12.4737586738
C20	2.8073389441	14.6590597865	11.0739288847
H21	3.3002030023	15.4359059561	10.4974336133
C22	2.3352067122	13.5218169906	10.4708398440
H23	2.4525266566	13.3816274186	9.4015454960
C24	1.6562427466	12.5352919774	11.2258750183
H25	1.2337143825	11.6723365902	10.7203894593
C26	1.4901806283	12.6726044329	12.5842266152
C27	2.0318697762	13.8163255295	13.2260363872
C28	0.6691588164	11.7262375992	13.3943700492
C29	-0.4799068241	12.2498232172	14.0625534836
H30	-0.7208739586	13.3065083520	13.9971418792
C31	-1.5637715547	11.3672000648	14.3087426163
C32	-1.4809313335	10.0481844162	14.0052454893
C33	-0.2935699003	9.4898295641	13.4904010255
H34	-0.2182943242	8.4092365741	13.4254586510
C35	0.7694846620	10.3026008257	13.1969449884
C36	2.0799031370	9.7161699415	12.8423633404
C37	2.1734744327	8.7531238002	11.8622576937
H38	1.2766895967	8.4730971840	11.3178954723
C39	3.4006865910	8.1356300875	11.5346726744
H40	3.4287729557	7.3861647522	10.7510450438
C41	4.5420576864	8.4933726631	12.1998743242
H42	5.4980226944	8.0369085337	11.9604820300
C43	4.4937578532	9.4739119607	13.2246593761
C44	5.6618420674	9.8463181083	13.9357014858
H45	6.6074066319	9.3733236739	13.6853040446
C46	5.5763024758	10.7871032634	14.9228582395
H47	6.4398435059	11.1023724815	15.4964353484
C48	4.3121980126	11.3480293720	15.2058200005
H49	4.2165534222	12.0822808284	15.9999879677

C50	3.2615881191	10.0998398406	13.5635539480

7. References

1. Bruker *Saint; SADABS; APEX3*, Bruker AXS Inc.: Madison, Wisconsin, USA., 2012.
2. Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2015,** *71*, 3-8.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42*, 339-341.
4. Sheldrick, G. CELL_NOW, Version 2008/4; Georg-August-Universität Göttingen: Göttingen, Germany, 2008.
5. Spek, A. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2015,** *71*, 9-18.